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A NEW STABILITY TEST FOR NITROCELLULOSE POWDERS.

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STABILITY tests, sometimes also called "heat tests," are applied to explosives to determine their stability or keeping qualities. During the process of manufacture these tests are made to determine if the product has been sufficiently purified, *i. e.*, freed from substances which might cause it to decompose spontaneously.

Before describing the new test, the more important and most used of the old tests, including the four used by the Ordnance Department, U. S. Army, are briefly mentioned; this is done so as to point out the weak points of these tests to those not familiar with them.

THE POTASSIUM-IODIDE-STARCH, OR ABEL TEST.

This test is prescribed and made by the Ordnance Department, U. S. A., as follows: 1.3 grains of the sample (air-dried) is placed in a test-tube in which there is suspended a test paper of potassium-iodide-starch, moistened to one-half its length with a 50 per cent. glycerin solution. This tube is then immersed in a bath kept at 65.5° C. ± 1°, for nitrocellulose, and at 100° C. ± 1°, for nitrocellulose powders. The test is ended at the appearance of a brown

or blue line on the test paper. For a good nitrocellulose this discoloration must not take place in less than forty minutes (at 65.5°), and for a good nitrocellulose powder in not less than ten minutes (at 100°). Powders containing nitroglycerin should stand this test for twenty minutes at 65.5°.

The discoloration of the test paper is due to the action of free iodine on the starch, the iodine being liberated from the potassium iodide by impurities or products of decomposition, principally oxides and acids of nitrogen volatilized from the explosive. This test is of some value to the manufacturer to determine whether his product has been thoroughly purified, and the test could be called "purity test" more appropriately than a stability test. When applied to finished products, this test has many weak points, as follows:

(1) It shows, in cases of decomposition of the sample during the test, only the beginning and not the continuation of the decomposition; it is more important to know how decomposition proceeds than when it begins.

(2) Traces of unstable nitro-compounds would show a nitrocellulose or powder in which they are found by this test to be bad; yet these traces of unstable compounds might not cause a decomposition of the explosive, if stored under ordinary conditions, and, considering that there is no indication of the effect of these unstable compounds, this test does not indicate the keeping qualities of the explosive.

(3) Traces of solvents left in a powder affect this test.

(4) The weakest point of this test is the fact that it can be masked by a number of substances which are sometimes added to the explosive for this purpose. These substances are mercuric chloride, mercury salts, carbonates, alkalies, amines, acetic ether, acetone, oils, vaseline, aniline, etc. Explosives containing masking substances are not accepted by the Ordnance Department.

(5) The test is affected by the condition of the sample, size of grains, whether freshly prepared for testing or exposed to air, and by moisture content. Charges of static electricity, which a powder acquires on rasping or cutting, affect the results of this test. Experiments along this line are being made by Capt. H. C. Aspinwall.

(6) Slight differences in test papers greatly affect the results of this test. (The test papers used by the Ordnance Department

are made in large quantities by Eimer and Amend, of New York, according to specification, thereby insuring greater uniformity than if made at different laboratories in small quantities. Manufacturers who have contracts with the government are supplied with these papers.)

(7) The personal equation of the operator enters as a factor in causing variations. It is no easy matter to decide just when there is the first appearance of a brown line on the test paper.

On account of the points mentioned, duplicates of the same powder have been known to vary from twenty to thirty minutes. The potassium-iodide-starch test has long been known to be unreliable, and the Ordnance Department condemns no explosives on results of this test alone.

THE ZINC-IODIDE-STARCH TEST.

This is a modification of the test just described, zinc iodide being used instead of potassium iodide (temperature 80° C.). Zinc iodide is more sensitive than potassium iodide, and also acts as a preservative of the test-paper. However, a greater sensitiveness is in no way an improvement of the potassium-iodide-starch test, and results obtained at this laboratory show that this test is not more reliable than the original, having all the weak points of the latter.

THE GUTTMANN TEST.

Instead of using a potassium-iodide-starch paper, Guttmann recommended[1] a test paper moistened with a solution of diphenylamine in sulphuric acid. He claimed for his test the following advantages: (1) Not as sensitive as the potassium-iodide-starch test; (2) test papers more easily prepared; (3) masking substances do not interfere. The temperature used is 70° C., and nitrous fumes turn the colorless paper to a greenish-yellow and finally blue.

Thomas says[2] the diphenylamine test is unsatisfactory; it may be masked by the addition of diphenylamine to the explosive to be tested. Guttmann himself admits that the blue color sometimes fails to appear. Moisture in the sample affects the test. Thomas as well as others failed to get a sharp end-reaction. The Guttmann test was tried at this laboratory but gave unsatisfactory results, and was discontinued. Aspinwall,[3] Spica,[4] and Thomas

[1] *Ztschr. angew. Chem.* (1897), p. 233; *J. Soc. Chem. Ind.* (1897), p. 283.
[2] *Ibid.*, (1898), p. 1027.
[3] *J. Soc. Chem. Ind.*, May 31, 1902.
[4] *Rivista*, August, 1899.

found sufficient objections, after trial, to discard it. Major Nathan says[1] the test fails when testing volatile explosives, such as nitroglycerin, the latter being decomposed by the sulphuric acid on the test paper.

THE HESS TEST.[2]

Nitrocellulose is heated to 70° C. in a tube and, by means of a current of air, the volatile products of decomposition are carried into a dilute potassium-iodide-starch solution. Five observations are made: four colorimetric readings on the potassium-iodide-starch solution, and the time required for explosion of the sample. This test shows the beginning, and roughly, and for a short time also, how decomposition proceeds. The potassium-iodide-starch solution, however, is far too sensitive, and may show decomposition which in reality does not indicate instability of the explosive. Masking substances interfere as mentioned under the potassium-iodide-starch test, and results are affected by solvents in the sample, condition of the sample, difference in the testing solution, and personal equation of the operator.

THE HOITSEMA TEST.[3]

The explosive is heated for fifteen minutes at a constant temperature, and then, by means of a current of carbon dioxide, the volatile products of decomposition are passed through glass wool moistened with Guttmann's diphenylamine solution. This operation is repeated, lowering the temperature 10° each time until a temperature is found at which no products of decomposition are found which give a color reaction with the test solution, this being considered the point at which decomposition ceases.

The test is too sensitive and subject to most of the objections mentioned under previous tests, especially under the Guttmann test.

THE EXPLOSION TEST.

A small sample of the explosive (usually 0.1 gram) is placed in a strong test-tube which is then tightly corked and placed in a paraffin bath at 100° C. The bath is now stirred and heated so that the temperature increases 5° per minute. The temperature is noted at which the sample explodes.

[1] *J. Soc. Chem. Ind.* (1901), p. 10.
[2] *Mitth. ü. Gegenst. d. Artill. u. Geniewesens* (1879), p. 345; Dingler's *poly. J.*, **234**, 43.
[3] *Ztschr. angew. Chem.* (1889), p. 705.

A good nitrocellulose should not explode under 186° C.

A good nitrocellulose powder should not explode under 177° C.

A good nitroglycerin powder should not explode under 170° C.

These explosion points are required by the Ordnance Department; those required by other governments differ considerably. Judging from a great number of explosion tests made at this laboratory it seems that this test is reliable when the explosive is either very good or very bad. Variations in results may be caused by difference in manipulation of the test, especially in raising the temperature; the following table shows the effect on the explosion point of raising the temperature 1°, 2.5°, and 5° per minute, on powders Nos. 175, 178, 179 and 180.

Powder.	1°.	2.5°.	5°.
175	164	174.5	177
178	170	176	178
179	173	176	177
180	167	174.5	179

This table also shows that greater differences between the explosion points are obtained when the temperature is raised only 1° instead of 5° per minute.

THE THOMAS TEST.[1]

In this test the sample is heated in a glass-stoppered tube in an oil-bath for eight hours daily. A good nitroglycerin powder should stand four days' heating at 94°-96° C. without developing brown fumes (N_2O_4); a good nitrocellulose and nitrocellulose powder should not show fumes before three days, using a temperature of 99°-101° C.

These temperatures are too low to produce a decisive decomposition which may be observed by the appearance of brown fumes; it is hard to say just when brown fumes appear. Varying amounts of moisture and solvents in the powder will give different pressures in the closed tube, and consequently different results, since pressure affects decomposition.

THE 135° C. TEST.

Two and one-half grams of the explosive, and a piece of blue litmus paper are placed in a strong test-tube (320x18 mm.); the latter is tightly corked and placed in a bath at 135° C. Three observations are made: (1) Reddening of the litmus paper, (2)

[1] *Zischr. angew. Chem.*, p. 1027 (1898).

brown fumes (N_2O_4), and (3) explosion of the sample. The minimum time as required by government specifications for these three observations is as follows:

	Litmus red.	N_2O_4.	Explosion.
Nitrocellulose	30 min.	45 min.	5 hrs.
Nitrocellulose powder	1 hr., 15 min.	2 hrs.	5 hrs.
Nitroglycerin powder	30 min.	45 min.	5 hrs.

After subjecting a large number of samples to this test it has been found that any one of these three observations alone is not always a correct indication of the condition or stability of the sample.

To illustrate:

	Litmus red.	N_2O_4.	Explosion.
Powder No. 445	1.30	3.30	None in 5 hrs.
Powder No. 265	2.05	2.45	3.25

Powder No. 445 is a good, stable powder, while No. 265 is unstable; yet the former reddened litmus paper before the latter. Again:

	Litmus red.	N_2O_4.	Explosion.
Powder No. 265	2.05	2.45	3.25
Powder No. 610	2.05	2.45	None in 5 hrs.

Here the first and second observations are alike, but No. 610 did not explode and was shown by other tests to be a perfectly stable powder. No. 265 is bad. These examples show that the reddening of blue litmus paper and the appearance of brown fumes in this test, as well as in all other tests where these observations are made, are not always reliable indications of the relative stability of powders. The temperature of 135° C. is usually considered too high for stability testing as it may cause decompositions not always dependent upon the stability. In this test it is sometimes difficult to decide when the litmus paper is red, and when there is the appearance of brown fumes; two operators may vary thirty minutes or even more in the observations of this test. Different makes of litmus paper give different results; the papers used by the Ordnance Department are made according to specifications by Eimer and Amend, and of as nearly uniform quality and sensitiveness as possible.

By keeping all conditions as nearly uniform as possible, this test becomes one of the best of its kind.

THE VIEILLE TEST.

Ten grams of the explosive are placed in a strong glass tube or bottle, a piece of blue litmus paper is placed above the sample and

the tube closed air-tight; the tube is then heated in an air-bath at 110° C. until the litmus paper is completely reddened. The time required for this reddening is noted, the bottle removed and opened; this operation is repeated daily until the time required to redden the litmus paper is one hour or less; of course a clean bottle and fresh paper is used each day. The daily times are added and the total (or accumulated) time should not be less than thirty hours for large powders (for 5-inch gun or larger), twenty hours for small powders (less than 5 inches), and ten hours for nitrocellulose. On account of the volatility and danger of explosion of nitroglycerin, powders containing it cannot be tested by this method.

The reddening of the litmus paper indicates only acid products of decomposition and is affected by the moisture-content of the sample. It is practically impossible to have all the Vieille bottles equally tightly closed; experiments have shown that pressure is an important factor in the decomposition of nitrocellulose. The personal equation of the operator affects the readings; varying results are obtained unless the litmus papers used are uniform. The papers used by the Ordnance Department are the same as described under the "135° test."

Results obtained by the Vieille test are reliable only when the explosive is very good or very bad.

THE WILL TEST.[1]

Nitrocellulose is decomposed at 135° C. and by means of a current of carbon dioxide, the products of decomposition are carried into a reduction tube containing a heated spiral of copper gauze; this reduces the nitrogen compounds to nitrogen gas which is measured over sodium hydroxide. The nitrogen is measured at regular intervals, and the rate of evolution is taken as an index of the decomposition. A nitrocellulose, which by this test gives equal quantities of nitrogen in equal intervals of time, is considered by Will to be in "the limit state of purification," and therefore as stable as possible. Considering the principle of this test, and in theory it should give better results than any of the other tests so far described.

Will's test was thoroughly tried by Mr. C. P. Beistle of this laboratory, no expense nor time being spared in setting up the

[1] *Mitth. a. d. Centralstelle f. Wissenschaft. Untersuch.*, December, 1900; *Neu Babelsberg*; also abst. *J. Soc. Chem. Ind.*, June 30, 1900.

rather elaborate and complicated apparatus required, and in conducting the test. The results obtained were unsatisfactory and the test was abandoned.

The following reasons are given as the cause of unsatisfactory results:

(1) The temperature 135° C. is too high for stability testing purposes.

(2) The decomposition is measured only by the nitrogen evolved.

(3) From Professor Will's experiments and diagrams it is not at all clear where to draw the line between a stable and an unstable product.

(4) The statement is made in Professor Will's report that for a certain nitrocellulose, heated for thirty hours and losing one-fourth its original nitrogen, the evolution of nitrogen in equal intervals of time was identical, while in another place it is stated that 10 grams of nitrocellulose gave four times the amount of nitrogen that was given off by 2.5 grams. This latter statement is correct, judging from our own experiments, but it contradicts the former, since the amount of unchanged nitrocellulose in the former experiment is constantly decreasing.

(5) It is practically impossible to buy or make carbon dioxide which is free from air; and as it is difficult to pass carbon dioxide through the apparatus at a uniform rate, the air-content of the gas gives rise to serious errors, and if the current be too fast it may cool the sample, and it will not be completely absorbed by the sodium hydroxide solution; if too slow, the gases of decomposition are not carried away fast enough, which may effect the decomposition, as stated by Professor Will.

(6) If the reduction tube and copper spirals are not heated sufficiently high, or the current of carbon dioxide is passed too fast, some of the products of decomposition may escape reduction.

(7) Unstable products are liable to explode, which might cause considerable annoyance both to the operator and the apparatus.

THE NEW TEST.

From a study of the old stability tests, and considering what such tests really ought to show, it must be apparent that none of those in use now are entirely satisfactory. At this laboratory,

NOTE.—For a more detailed description of these tests and illustrations of apparatus, see article by the writer in *Journal of the Franklin Institute*, March, 1903.

explosives are subjected to the potassium-iodide-starch test, explosion, 135° C., and Vieille tests; having made these tests on each sample received, it is unlikely that a really unstable or dangerous explosive has ever been or ever will be accepted. But contradictory results are often obtained (see Table I), due to weak points of these tests.

During a series of experiments for Captain B. W. Dunn, Ordnance Department, U. S. Army, to examine the behavior of powders when subjected to higher temperatures it was noticed that for the same temperature there is a great variation in the behavior of different powders. (Credit is due to Captain Dunn for suggestions and aid in this work.)

If the decomposition of powders increases as the temperature increases, then the behavior of these powders at higher temperatures is an index of their behavior at low temperatures. To prove the relation between temperature and decomposition, a number of powders were heated on watch-glasses in air-baths regulated to different temperatures; at regular intervals the samples were cooled in a desiccator, weighed, and the percentage of loss, due to decomposition and volatilization, calculated. In this series of experiments, powder No. 179, a good nitrocellulose powder, was subjected to temperatures[1] of 80°, 100°, 110°, 115° and 135°; the losses at these temperatures are shown in Fig. 1. After the loss of moisture and solvents, the volatilization of the powder proceeds relatively slowly, but with an increasing rate until a condition is reached which corresponds to the breaking-point of the powder, the action being similar in many respects to that of a metal test specimen in passing its elastic limit. The new test promises to give us, then, *The Elastic Limit of Powder Resistance to Heat*, and this is the new measure proposed for the powder's stability. In Fig. 1, the 110° and 115° curves locate this elastic limit more definitely than the others, the 110° curve at 12, and the 115° curve at 8 days. It is also located at 12 days by the 100° curve, but this temperature is evidently too low. It was not located in thirty days by a temperature of 80°. At 135° no initial stage of resistance could be detected, and it is assumed that at this temperature all powders begin to break down immediately. From the curves on Fig. 1, it is apparent that the best temperature for determining the elastic limit of a normal powder is about

[1] All temperatures are °C.

TABLE I.

Laboratory No. of powder.	Size of grain (inch).	Potassium iodide starch test.			135° C. test.				New 115° C. test.		
		Original. Min.	One year later. Min.	Explosion. Test C.	Litmus red.	N_2O_4.	Explosion limited to 5 hours.	Vieille test. Hr., min.	Daily loss exceeded 1 per cent.	Maximum daily loss.	Total loss for 6 days. Per cent.
4–11	0.25 × 0.5	15	15	174	1 : 40	None	None	....	7th day	12th day	6.52
4–25	0.56 × 0.7	39	30	171	1 : 52	None	None	....	From beginning	8	10.22
155	0.62 × 1.0	16	13	...	2 : 00	None	None	27 : 20	Not reached	Not reached	4.72
179	0.25 × 0.6	35	23	177	4 : 00	None	None	27 : 05	9	13	5.34
197	0.25 × 1.0	..	12	176	1 : 55	None	None	19 : 40	9	Not reached	4.73
210	0.7 × 1.7	28	11	177	2 : 50	None	None	49 : 40	12	14	7.16
262	0.45 × 1.12	18	12	172	3 : 00	None	None	49 : 15	Not reached	Not reached	7.45
265	0.8 × 1.8	15	10	171	2 : 05	2 : 45	3 : 25 3 : 55	29 : 05	From beginning	8	12.54
293	0.8 × 1.8	15	11	166	1 : 20	2 : 20	None	33 : 30	From beginning	7	15.89
294	0.7 × 1.7	10	7	177	2 : 15	None	None	46 : 25	14	Not reached	6.88
326	0.45 × 1.5	30+	30+	161	: 50	2 : 47	3 : 00 4 : 00	24 : 40	From beginning	6	19.70
344	0.7 × 2.0	13	13	150	1 : 15	2 : 22	3 : 00 4 : 15	25 : 10	From beginning	5	19.39
373	0.75 × 1.6	30+	5	175	2 : 35	None	None	36 : 50	13	16	6.44
387	0.4 × 0.9	9	30+	174	3 : 20	None	None	22 : 50	11	Not reached	5.11
389	0.4 × 0.75	10	..	178	1 : 00	None	None	12 : 40	Not reached	Not reached	5.49

TABLE I.—(*Continued*).

389	0.4 × 0.75	10	..	178	1 : 00	None	None	12 : 40	Not reached	Not reached	5.49

TABLE I.—(*Continued*).

Laboratory No. of powder.	Size of grain (inch).	Potassium iodide starch test. Original. Min.	Potassium iodide starch test. One year later. Min.	Explosion. Test C.	135° C. test. Litmus. red.	135° C. test. N_2O_4.	135° C. test. Explosion limited to 5 hours.	Vieille test. Hr., min.	New 115° C. test. Daily loss. exceeded. 1 per cent.	New 115° C. test. Maximum daily loss.	New 115° C. test. Total loss for 6 days. Per cent.
391	0.25 × 0.36	12	18	168	: 50	1 : 45	2 : 45 2 : 50	8 : 35	From beginning	5	21.55
396	0.65 × 1.7	20	12	173	3 : 20	None	None	21 : 45	14	Not reached	8.53
405	0.75 × 1.6	30+	17	175	2 : 00	None	None	19 : 15	From beginning	6	18.14
406	0.36 × 1.0	30+	30+	168	1 : 15	3 : 40	3 : 55	15 : 45	From beginning	6	18.80
407	0.6 × 1.3	30+	30+	167	1 : 50	2 : 25	2 : 35	15 : 50	From beginning	7	12.00
445	0.42 × 0.9	15	30+	176	1 : 30	3 : 30	None	31 : 40	11	17	4.83
544	0.25 × 0.63	21	14	176	2 : 15	None	None	30 : 20	Not reached	Not reached	5.11
546 F.A.	0.45 × 1.5	12	30+	170	1 : 20	None	3 : 00 3 : 40	6 : 50	From beginning	3	25.64
577	0.34 × 1.0	12	..	175	1 : 10	1 : 45	None	21 : 45	9	Not reached	6.74
608	0.12 × 1.0	30	..	175	1 : 10	4 : 30	None	16 : 05	6	10	6.05
610	0.8 × 1.8	16	10	178	2 : 05	2 : 45	None	30 : 35	14	Not reached	6.58
619	0.4 × 0.9	6	..	176	2 : 10	3 : 50	None	31 : 15	12	17	5.44
716	0.4 × 0.6	10	..	175	1 : 25	None	None	22 : 00	Not reached	Not reached	4.53
717	0.4 × 0.6	10	..	172	1 : 00	None	None	18 : 55	Not reached	Not reached	5.23

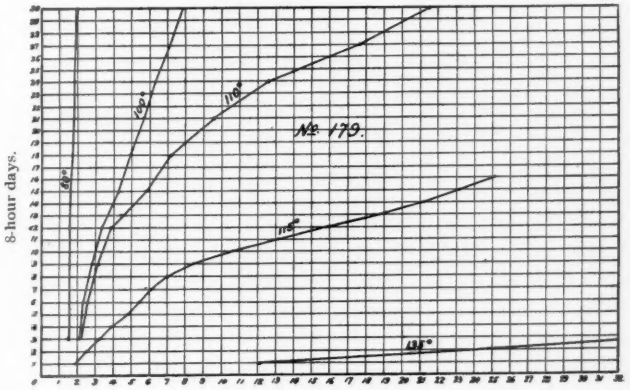
TABLE I.—(*Continued*).

Laboratory No. of powder.	Size of grain (inch).	Potassium iodide starch test.		135° C. test.				Vieille test. Hr., min.	New 115° C. test.		
		Original. Min.	One year later. Min.	Explosion. Test C.	Litmus red.	N_2O_4.	Explosion limited to 5 hours.		Daily loss exceeded 1 per cent.	Maximum daily loss.	Total loss for 6 days. Per cent.
797	0.4 × 0.75	55	..	175	2 : 15	None	None	25 : 40	Not reached	Not reached	5.69
798	0.4 × 0.75	45	..	179	2 : 15	None	None	24 : 50	12	Not reached	4.77
799	0.4 × 0.75	60+	..	177	2 : 30	None	None	22 : 30	10	Not reached	4.32
800	0.62 × 1.0	30+	..	178	2 : 05	None	None	31 : 25	Not reached	Not reached	4.85
803	0.8 × 1.8	27	..	173	1 : 50	3 : 20	3 : 25 3 : 30	24 : 15	From beginning	9	12.37
834	0.4 × 0.87	30+	..	171	3 : 10	None	None	19 : 50	11	Not reached	5.90
836	0.48 × 0.95	30+	..	175	3 : 30	None	None	30 : 45	13	Not reached	7.07
922	0.75 × 1.12	15	..	177	2 : 00	2 : 45	None	31 : 00	Not reached	Not reached	5.00
924	1.0 × 1.75	10	..	175	1 : 40	2 : 45	None	31 : 10	Not reached	Not reached	5.50
926	1.12 × 2.0	10	..	179	2 : 05	3 : 25	None	31 : 00	Not reached	Not reached	5.99

115°. Fig. 2 shows 100°, 110° and 115° curves for a bad powder, No. 391. The elastic limit at 110° is located at nine days, and at 115° at three days. These results (shown in Figs. 1 and 2) prove that there is a definite relation between decomposition and temperature. They show also that a bad powder (No. 391) decomposes much faster, reaching the elastic limit sooner than a good one (No. 179) at the same temperature; after forty-eight hours' heating at 115°, No. 391 lost 21.55 per cent., while No. 179 lost only 5.34 per cent.

The relation between temperature and decomposition, and the fact that a bad powder decomposes faster than a good one having been proved by these results, it remained to be decided which temperature is best suited to distinguish a bad from a good powder. This required a long series of experiments. It is obvious, of course, that the lower the temperature used, the more nearly does the test approach conditions to which a powder is liable to be subjected during storage and handling; but, the higher the temperature used, the shorter will be the time required to show sufficient decomposition to distinguish between a good and bad powder. Although it is very desirable to shorten the time required for making a test, it is not advisable to sacrifice accuracy on this account.

As may be seen from Fig. 1, the decomposition of a powder at 80° is exceedingly slow; even at 100° it is still very slow (Figs.



Per cent. loss.
Fig. 1.

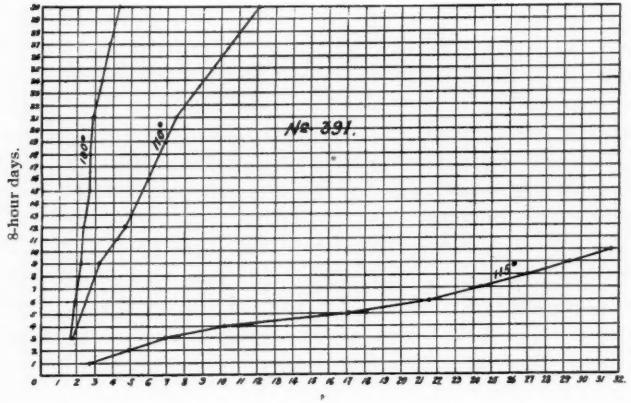


Fig. 2.

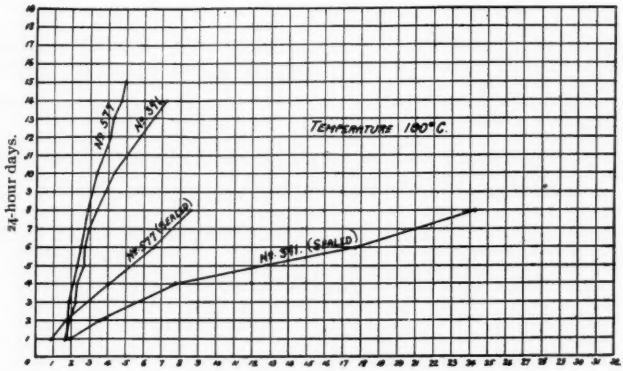


Fig. 3.

1, 2 and 3), but the difference between a good and bad powder becomes quite noticeable at 100°, as shown in Fig. 3 by No. 577 (good) and No. 391 (bad). However, the difference is not sufficient, and the time required is too long to be used as a practicable test. Decomposition is greatly increased at 110°, and the difference between good and bad powders becomes greater; this is shown in Fig. 4, where Nos. 619, 445 and 577 are very good, and Nos. 391, 326 and 546 F. A. are very bad powders, the others

shown being intermediate. Here again the time required to show the differences is still quite long, too long for practical testing.

The temperature was next increased to 115°, and, in order to avoid possible danger from explosions, the exposures were made for eight hours only (during working hours); at the lower temperatures the tests were allowed to run during the night. Three grades of powders were used for all tests—good, bad, and intermediate or doubtful. At 115°, decomposition takes place rapidly, and the difference between good and bad powders becomes apparent in a few days as shown in Figs. 5, 6 and 7, which will be more fully discussed later.

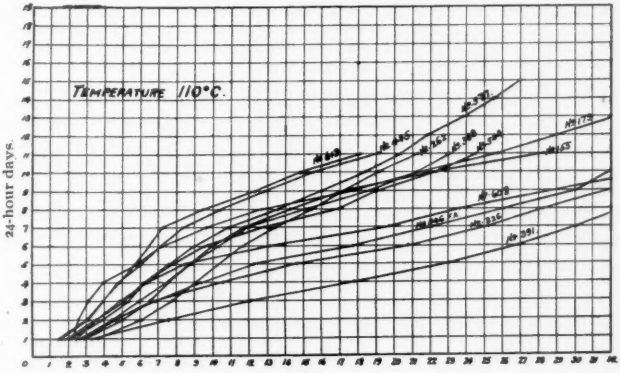


Fig. 4.

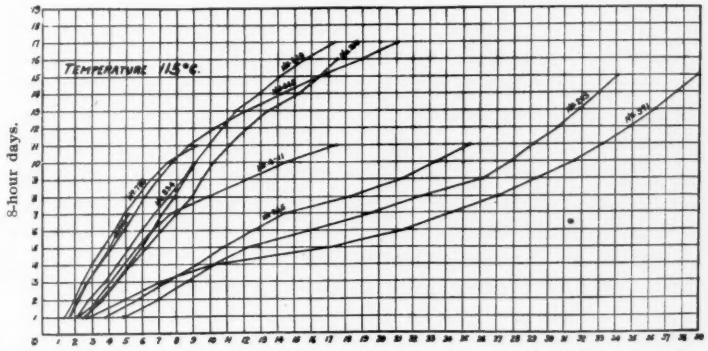


Fig. 5.

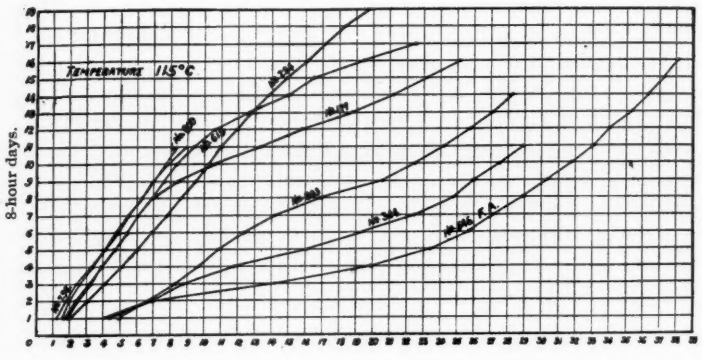


Fig. 6.

Some experiments were made at 120°; the rate of decomposition increased at this temperature, but the difference between a good and bad powder did not seem as great as at 115°, all powders decomposing more or less rapidly at 120°.

Experiments were made to determine the combined effect of heat and pressure on powders; the weighed samples were placed in small tin boxes and the latter sealed (soldered) air-tight; they were then exposed to 80° and 100°, the boxes opened and weighed at regular intervals. At 80° decomposition is slow, but more rapid than if the powder were heated in the open on a watch-glass, *e. g.*, No. 179 heated at 80° lost 9.90 per cent. in forty-one days when sealed, but lost only 2.85 per cent. when heated on a watch-glass at the same temperature and for the same length of time. For a reasonably short time of exposure the difference between a good and a bad powder at 80°, sealed, is small. At 100°, sealed, the difference between a good and bad powder becomes quite marked, as may be seen from Fig. 3; this figure also shows that the difference between a good (No. 577) and a bad powder (No. 391) is greater when sealed and decomposed under pressure than when heated in the open; the time required is also reasonably short. It will be observed that the effect of pressure is the same as that of an increase in temperature. It is probable that more extensive experience may result in the adoption of a "sealed" method of testing. A form of holder must be devised, however, better than the bottles used in the Vieille test. The sealing features of this holder must be reliable and convenient. It will

probably be of metal with a convenient method of sealing by pressure derived from a screw thread, and not depending upon a rubber gasket. In addition to shortening the time required for tests at a given temperature, the sealing method is preferred because it corresponds more nearly to the conditions of storage of powders. In fixed ammunition the powder charges are almost if not quite hermetically sealed to make the ammunition water-proof, and when stored in large metal-lined boxes in magazines the quantity of powder is very large as compared with test specimens, and the space for the volatile matter to collect very small. It is intended to hermetically seal the storage cases by soldering.

From these preliminary experiments it appeared that when heating the powders unconfined, 115° gave the best results. Considering the importance of a knowledge of the stability of a powder, the time required to get results at 115° may be considered reasonably short.

For some of the preliminary tests an ordinary sheet-copper

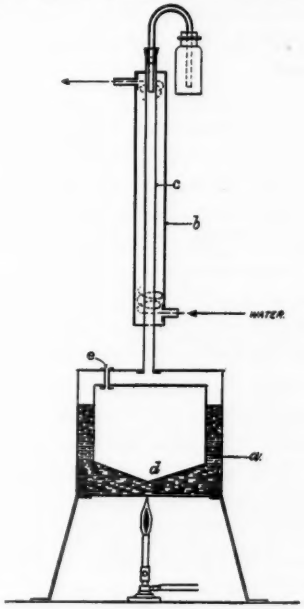


Fig. 7.

air-bath or oven was used; the temperature was regulated

by means of a gas regulator or thermostat; however, it was a matter of considerable difficulty to keep the oven at 115°, and under the most favorable conditions it was impossible to avoid variations of + or —1° or 2°. In order to obtain a more uniform temperature, an oven shown in Fig. 1 (diagrammatic sketch) was devised. The oven part is double-walled, of heavy sheet-copper, similar to the ordinary double-walled water-ovens; but in order to prevent bumping and jarring, which is a common fault of all water-ovens, the bottom part of the inner wall was made slightly V-shaped; this arrangement causes the contents of the oven to boil quietly, and effectively prevents bumping. A reflux condenser in the top of the oven prevents the volatilization of the boiling mixture. The latter consists of commercial xylene and toluene in such proportion that when the mixture is boiling, the temperature of the air on the inside of the oven is 115°. This arrangement is simple and has been found perfectly satisfactory, the temperature varying less than 0.5° + or —. The opening *E* is for a thermometer; the oven has two shelves, and an opening (closed by a screw plug) for introducing the xylene-toluene mixture; these are not shown in the sketch.

The test adopted, pending further developments, is as follows: From one to four whole pieces of the powder to be tested are weighed on a watch-glass and heated for eight hours in the 115° oven; the sample is allowed to cool in a desiccator and weighed; the loss in weight is calculated to percentage. This is repeated from day to day until completion of test (6 days, or less).

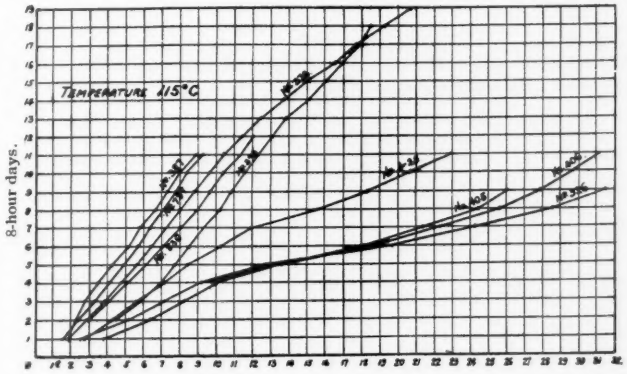
A large number of powders have been subjected to this method of testing, and some of the results are shown in Figs. 5, 6 and 7. In Fig. 5 the powders numbered 391, 293 and 265 are bad, 4-11 are doubtful, while the others are good. In Fig. 6, Nos. 546 F. A., 344 and 803 are bad, the others are good. In Fig. 7, Nos. 326, 406 and 405 are bad, 4-25 are doubtful, while the others are good. The powders indicated as bad had previously been diagnosed as such by a careful study of the combined results of four of the old stability tests (see Table I).

In the new test at 115° during the first day's heating, a good powder loses approximately its moisture and volatile matters; after this, the daily loss is less than 1 per cent., but gradually increases until a maximum is reached, after which it slowly decreases. The daily loss of a good powder does not exceed 1 per

cent. before the sixth day, often not before the tenth day. The maximum daily loss is usually not reached before the eighth day. A bad powder usually loses more than its moisture and volatile matters on the first day; the daily loss is more than 1 per cent. before the sixth day and the maximum daily loss occurs before the eighth day.

The total loss of a good powder for six days is less than 10 per cent.; bad powders lose considerably more than 10 per cent. in six days. By this test, therefore, it is possible to obtain reliable indications as to the stability of a powder in six days of eight hours each. In special cases where it is necessary to get results more quickly, the exposures could be made for twenty-four hours, or weighings could be made at eight-hour intervals, and results obtained in a little over two days.

After prolonged heating, good and bad powders approach the same total loss (Fig. 8). Preliminary analyses of the residues



Per cent. loss.

Fig. 8.

from these heat tests indicate that the decomposition of the powders by heat is a complex reaction or process. Most powders become quite brittle and porous but still retain their shape, the decomposition being a sort of destructive distillation; a few powders, usually bad, lost their shape, being fused and soft while hot, porous and brittle when cold. The percentage of nitrogen decreases as the total loss increases. With a total loss of 55 to 56 per cent. the nitrogen in the residue was found to be 4.31 to

4.91 per cent. (15 samples examined; original nitrogen 12.37 to 12.60 per cent.). This agrees with the fact that the loss curves

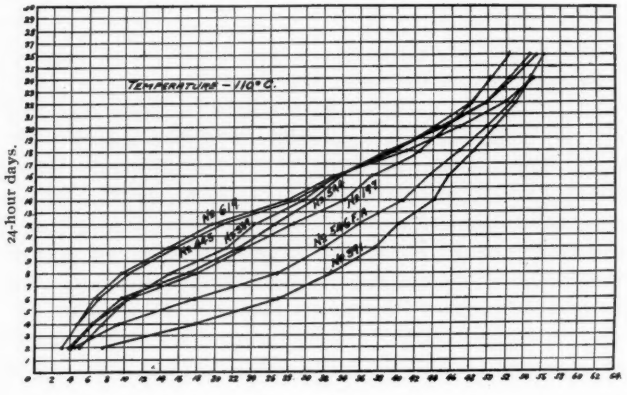


Fig. 9.

(Fig. 8) are close together at 55 to 56 per cent. "Acetone insoluble" nitrocellulose increases with total loss:

Total loss. Per cent.	"Acetone insoluble" nitrocellulose. Per cent.
41.37	0.12
55.67	0.72
65.08	6.99

Analysis of residues as well as volatile products of decomposition

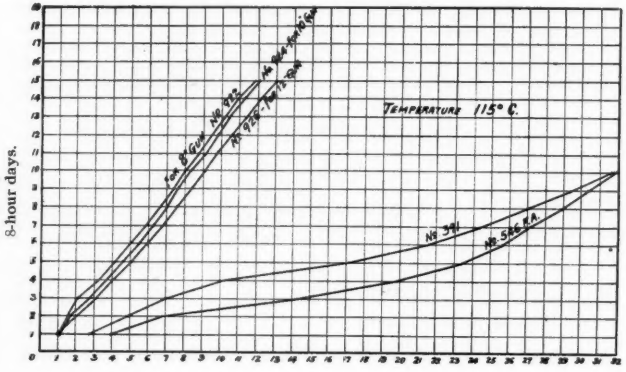


Fig. 10.

is to be the subject of future investigation. The size of the grain of powder affects the decomposition slightly, but not sufficiently to be taken into consideration when distinguishing a bad from a good powder by this test; decomposition of a powder increases slowly as the size of the grain increases; this is shown in Fig. 9. Powders Nos 922, 924 and 926 are made from the same lot of nitrocellulose, as nearly alike as possible, except in size as indicated in Fig. 9. Powders Nos. 391 and 546 F. A. are bad powders, shown for comparison.

Results of four old stability tests, and of the new test, are shown in Table I. A study of this table shows that the old tests often give contradictory results, due to weak points of these tests as pointed out in their description. The requirements for a good or stable powder by the old tests are, for

Potassium-iodide-starch test, 10 minutes.
Explosion test, 177° C.
135° test { Litmus red, 1.15.
N_2O_4 fumes, 2.00.
Explosion, none in five hours.
Vieille test { Twenty hours for five-inch powders.
Thirty hours for powders larger than five-inch gun.

Table II, made from Table I and the above requirements, shows how results from the old tests often contradict each other as well as that obtained from the new test: the new test is always corroborated by one or more of the old tests.

TABLE II.

No.	New 115° test.	Potassium-iodide-starch test.	Explosion test.	130° test.	Vieille test.
293	Bad	Good	Bad	Good	Good
294	Good	Bad	Good	Good	Good
326	Bad	Good	Bad	Bad	Bad
344	Bad	Good	Bad	Bad	Bad
396	Good	Good	Bad	Good	Bad
405	Bad	Good	Bad	Good	Bad
619	Good	Bad	Bad	Good	Good
717	Good	Good	Bad	Good	Bad
834	Good	Good	Bad	Good	Bad

The new test has the following advantages over the old method:

(1) The powder is tested in its natural condition.

(2) It shows all products of decomposition; the old tests show only acid products, or, the Will test, only nitrogen.

(3) It shows the decomposition of nitro-compounds other than nitrocellulose which are often present in a finished powder, and it also shows the effect of this decomposition on the powder itself.

(4) It shows the effect on the stability of a powder, of small quantities of added substances (for masking stability or other purposes); volatile matter; handling and working which may set up local decomposition; traces of nitrating acids due to imperfect purification; decomposition due to saponification[1] by water, alkalies, carbonates, etc.

(5) It shows quantitatively the progress of all decomposition.

(6) The test itself, as well as the apparatus, is simple and not subject to variations like the old tests.

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A STUDY OF THE DOUBLE CYANIDES OF ZINC WITH POTASSIUM AND WITH SODIUM.

BY W. J. SHARWOOD.

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DURING the precipitation of gold and silver by means of metallic zinc, from the solutions obtained in the cyanide process of extracting precious metals from their ores, more or less zinc is dissolved and accumulates to a certain extent in these solutions, and its presence in some instances modifies or complicates the estimation of the simple alkaline cyanide in such solutions, and also slightly affects their subsequent action on some of the constituents of the ores or other materials treated by them.

A typical solution might have originally contained one-fourth of 1 per cent. of potassium cyanide, to which about the same amount of calcium hydroxide or sodium hydroxide might be added, after which, with occasional additions of the same reagents, it has been filtered alternately through pulverized ore and finely divided metallic zinc, several tenths of a per cent. of which might be found in the final solution. Some discussion has arisen as to the forms in which the zinc and cyanogen may be distributed in such a solution, whether, for instance, the zinc is in the form of a zincate (K_2ZnO_2) or a double cyanide (K_2ZnCy_4). The latter opinion has been more generally favored, but after a cyanide solution has been in use for some months—judging from the published analyses

[1] Thomas: *Ztschr. angew. Chem.*, (1899), p. 55.

of others as well as those made by the writer—the zinc will usually be found considerably in excess of the ratio of 1 atom zinc to 4 equivalents of cyanogen, that is, of the cyanogen contained in simple alkaline cyanides plus that in the double zinc cyanide, although the solution may still have an excellent solvent action on the precious metals and may still show the same percentage of "available" cyanogen by the usual methods of titration with silver nitrate, which was formerly supposed to indicate only that portion of the potassium cyanide which was uncombined with zinc and so available as a gold solvent.

A. James[1] proved that when equivalent weights of crystallized potassium zinc cyanide and caustic potash were mixed and evaporated, the crystals deposited were still almost pure double zinc cyanide and contained practically all the cyanogen present, and that the same compound separated out when potassium zincate was mixed with a potassium cyanide solution and evaporated. The writer has confirmed these results, and also found that almost any compound of zinc, dissolved in almost any proportion in potassium cyanide, will similarly deposit crystals of potassium zinc cyanide, proving that, *in saturated solutions,* this is the compound which tends to form, whether by virtue of greater stability or lesser solubility. In the dilute solutions met with in metallurgical work the conditions may be different, but it is difficult to prove, for instance, in a solution containing potassium, zinc, and cyanogen in the proportions corresponding to $6K + Zn + 4Cy$, whether it actually contains $K_2ZnO_2 + 4KCy$ or $K_2ZnCy_4 + 4KOH$, as the results of titration or of gravimetric analysis would be the same in either case, and there seems to be no direct method of settling the question.

Some attempts were therefore made to decide this point by indirect means, to investigate more thoroughly the reactions which take place when various zinc compounds are dissolved in solutions of alkaline cyanides, or zinc cyanide in caustic alkalies, and to determine whether there is any appreciable difference in the effects of sodium and of potassium compounds in this direction, as might be inferred from the different constitutions assigned by Rammelsberg (K_2ZnCy_4 and $NaZnCy_3$) to the double cyanides of zinc with these metals. The results of the work in

[1] *J. Soc. Chem. Ind.*, **16**, 120 (1897).

this connection on the solvent action of zinc potassium cyanide solutions on gold have been already published.[1]

METHODS OF ANALYSIS.

In the analyses necessary for this investigation the only determinations required were those of zinc, cyanogen, and alkali, carbonate being the only impurity present in quantity. In the crystals examined, water and alkali-metal were also weighed.

Water was estimated by heating the crystals to 110° C. until constant weight was attained.

Zinc was determined by decomposing with hydrochloric acid, heating to expel any hydrocyanic acid present, neutralizing with sodium hydroxide, then adding a constant quantity (3 cc.) of strong hydrochloric acid, diluting to 150 or 200 cc. and titrating with a weak solution of potassium ferrocyanide, using uranium acetate as indicator, the titration being carried out in a hot solution, and a correction (0.3 cc.) being deducted for the quantity necessary to color the indicator.

Cyanogen was estimated by dissolving in or adding ammonia, and titrating with standard silver nitrate, using potassium iodide as an indicator. When zinc was present, an excess of sodium hydroxide was also added, and when present in proportions approaching Zn:4Cy an addition of one part in 200 was made to the cyanogen found by titration, that correction having been found necessary by previous experiments.

Alkali (potassium or sodium cyanide or hydroxide) was titrated by standard sulphuric acid, using phenolphthaleïn as an indicator, or, in some cases, methyl orange. In most instances, excepting the earlier experiments, carbonates had been removed from the solutions by means of lime, and, when the alkalinity of simple alkali-metal cyanide was found to exceed that due to the cyanogen present, the slight excess of alkali was usually neutralized by addition of standard acid in small quantity.

Sodium and potassium were gravimetrically determined, in some instances, as sulphates.

The probable composition of the solutions was calculated as follows: If the zinc present exceeded the ratio Zn:4Cy all cyanogen was reckoned as K_2ZnCy_4, the remaining zinc as K_2ZnO_2, and residual potassium as KOH. If the zinc present were below the amount corresponding to the ratio Zn:4Cy, zinc was reckoned as K_2ZnCy_4,

[1] *Eng. and Min. J.*, **64**, 396, 426, 460.

the remaining cyanogen as KCy, and residual potassium as KOH. In the few cases in which zinc was in excess of the ratio Zn:2K, the excess of zinc was calculated as $ZnCy_2$ and the remainder as K_2ZnCy_4 and K_2ZnO_2.

PREPARATION OF ZINC CYANIDE.

The standard methods recommended for its preparation are the precipitation of a zinc salt in solution by means of potassium cyanide (any carbonate in which coprecipitates zinc carbonate), and passing hydrocyanic acid into a solution of zinc acetate, when zinc cyanide separates. Special precautions are said to be necessary.[1]

According to Gmelin's "Handbook" the cyanide precipitated by the first method contains:

	From strong solutions. Per cent.	From weak solutions. Per cent.
$ZnCy_2$	89.9	54.4
ZnO	9.0	37.32
H_2O	2.0	8.25
	99.9	99.97
Whence the percentage of the total zinc present		
in the form of $ZnCy_2$ is	87.2	50.2
in the form of ZnO	12.8	49.8
and the approximate composition is	$7ZnCy_2.ZnO$	$ZnCy_2ZnO$.

Two attempts were made to prepare zinc cyanide by passing hydrocyanic acid into zinc acetate solution, but the amount of precipitate obtained was relatively small, and action seemed to cease at an early stage, presumably owing to the acetic acid set free preventing further action by the hydrocyanic acid, or redissolving the precipitate.

A 10 per cent. solution of purified zinc sulphate crystals was then precipitated by a 5 per cent. solution of "98 per cent. potassium cyanide" containing also sodium cyanide and carbonate, the zinc being kept in slight excess; the precipitate was washed free from sulphate. It was found to consist of a mixture of zinc cyanide with some zinc carbonate and a large proportion of zinc oxide or hydroxide.

[1] Gmelin's "Handbook," (1854 ed.), Vol. VII, p. 422; Corriol and Berthemot: *J. Pharm.*, **16**, 444; *Br. Arch.*, **35**, 153; *Repert*, **36**, 106; Bette: *Ann. Pharm.*, **31**, 214; Henry: *J. Pharm.*, **15**, 57; Schindler: *Mag. Pharm.*, **36**, 67; Wittstein: *Repert.* **63**, 314; Rammelsberg: *Pogg. Ann.*, **42**, 114; Joannis: *Compt. Rend.*, **92**, 1338, 1417; Wohler: *Berz. Jahresl.*, **20**, 152; Oppermann: *Jahresb. d. Chemie* (1860), p. 226; Varet: *Compt. rend.*, **105**, 170; *Ann. chim. phys.*, [7], 105 (1897).

A second lot was similarly prepared, but the cyanide was first carefully freed from carbonate by means of lime, and freshly boiled distilled water was used in dissolving and washing. This precipitate was found practically free from carbonate but only 58 per cent. of the zinc present was in the form of $ZnCy_2$, the remainder being presumably oxide or hydroxide. A third precipitation gave 55 per cent. of the zinc in the form of cyanide. In these and several other experiments it was found that the zinc cyanide lost cyanogen on washing, becoming more and more basic,[1] the wash-water smelling of hydrocyanic acid; after long washing, the zinc in the form of $ZnCy_2$ approximated 50 per cent. of the total zinc present, indicating the composition $ZnO.ZnCy_2$. This can be rapidly estimated by shaking up the precipitate, taking out two equal portions of the emulsion with a pipette (2 cc. if thick, or proportionately more if much water is present) and estimating zinc in one and cyanogen in the other by titration with ferrocyanide and silver nitrate respectively.

It is difficult to wash freshly precipitated zinc cyanide; it settles very slowly in water and will pass through any filter-paper; this may be remedied to some extent by adding about 5 per cent. of sodium sulphate to the first wash-waters, after which it settles fairly well, so that the water can mostly be decanted or siphoned off after five or ten minutes' standing.

On attempting to dry the precipitate there is always some decomposition, ammonia being formed for one thing; on allowing it to stand in the moist state, some ammonia is also developed.

The best results in preparation were obtained by first roughly precipitating a quantity of zinc cyanide by acting on zinc sulphate with carbonate-free alkaline cyanide; then adding to the roughly washed precipitate more alkaline cyanide—slightly in excess of the amount required to redissolve it. The resulting double cyanide solution was filtered clear, titrated to determine the amount of acid necessary to decompose the alkaline cyanide and liberate $ZnCy_2$, and then the whole was decomposed by a slight excess of sulphuric acid, added with constant stirring. The precipitation must be carried on in a good draft to avoid trouble with the hydrocyanic acid evolved. The vessel was then covered and allowed to stand till most of the precipitate had settled; the

[1] Although the reaction $ZnCy_2 + H_2O = ZnO + 2HCy$ (dissolved) is said to absorb 13 to 16 heat units.

bulk of the clear liquor was poured off and the precipitate washed several times with water, the first one or two lots containing a little free acid. This insures the evolution or presence of some hydrocyanic acid and counteracts the tendency of the water to hydrolyze the cyanide and render it basic. In one case, the washing was conducted with a solution of hydrocyanic acid.

Prepared in this way the proportion, by weight, of zinc to cyanogen is almost exactly 5 : 4, or practically all the zinc is in the form of cyanide. The product thus obtained, kept as an emulsion, is alluded to as "pure zinc cyanide"; that obtained in earlier tests and approaching the composition $ZnO.ZnCy_2$ as "basic zinc cyanide."

PREPARATION OF PURE CRYSTALLIZED POTASSIUM ZINC CYANIDE, K_2ZnCy_4.

This salt crystallizes readily in regular octahedra, and was easily prepared in solution by several methods.[1] It was obtained in a nearly pure form by first precipitating an impure basic cyanide by treating zinc sulphate with commercial "98 per cent." cyanide, containing about one-third sodium and two-thirds potassium cyanide, adding to the washed precipitate enough of the same cyanide in a hot solution to nearly redissolve it, filtering, cooling and allowing to crystallize, then recrystallizing the product three times by rapidly cooling a hot solution. The small crystals formed were thrown on a filter and sucked dry by a vacuum pump, washed twice with cold water and sucked dry; finally they were dried on filter-paper and kept some days over sulphuric acid. Water was estimated by drying at 110° C. to constant weight; on further heating there was no appreciable loss short of fusion. No sodium was detected.

	Calculated for K_2ZnCy_4. Per cent.	Found. I.	II.	III.	IV.	Average.
Potassium	31.56	31.49	....	....	...	31.49
Zinc	26.39	26.16	26.16	26.32	....	26.22
Cyanogen	42.05	41.88	41.88	41.77	41.77	41.82
Water	0.00	0.20	....	....	....	0.20
	100.00					99.73

The composition found by analysis, therefore, agrees precisely with

[1] Gmelin's "Handbook," Vol. VII, p. 422; Rammelsberg: *Pogg. Ann.*, **42**, 112 (1837); Fresenius and Haidlin: *Ann. Chem.* (Liebig), **43**, 132; Sharwood: *Eng. Min. J.*, October 9, 1897; Schindler: *Mag. Pharm.*, **36**, 67.

the percentage composition calculated from the formula assigned by Rammelsberg, whose determinations for zinc varied from 25.25 to 26.379.

SOLUBILITY.

This salt is stated in Comey's "Dictionary" to be "easily soluble in cold water." The mean of three determinations on the crystals above described gave a solubility of almost exactly 11 grams of potassium zinc cyanide in 100 cc. of water at a temperature of 20° C., but there is some tendency to form supersaturated solutions, and at higher temperatures the solubility is considerably greater. Only a minute trace was found to be dissolved by 100 cc. ethyl alcohol of specific gravity 0.798 (99 per cent.) at 20° C. In wood spirit, turpentine, ether, chloroform, acetone, carbon disulphide, coal oil and gasoline it was found to be completely insoluble.

On boiling a dilute water solution of this salt it is not precipitated, and carbonic acid is almost without effect upon the solution.

SODIUM ZINC CYANIDES, Na_2ZnCy_4 and $NaZnCy_3 + 2\frac{1}{2}H_2O$.[1]

The only reference found to the double sodium-zinc cyanide was that of Rammelsberg,[2] also quoted by Gmelin's "Handbook," Vol. VII, p. 422.

Rammelsberg says, in effect: "It was prepared in the same way as the potassium salt (acting on zinc cyanide) by means of sodium cyanide. The latter was obtained by saturation of pure (strong) hydrocyanic acid with lime, and decomposition of the calcium cyanide with sodium carbonate. The solution of the double zinc (sodium) cyanide leaves first, on strong concentration, glittering white leaflets, the precise form of which could not be determined. The properties of this salt are in general those of potassium zinc cyanide, but it is very readily soluble in water, and holds water combined; this, however, it loses, as it seems completely, at 200° C. The loss of weight in two analyses shows 21.71 and 23.88 per cent.

"Analysis of the desiccated salt shows:

(1) 0.458 gram gave ZnO 0.2194 = Zn 0.17584; Na_2SO_4 0.21 = Na 0.068478.

(2) 0.51 gram gave $ZnSO_4$ 0.475 = Zn 0.190695; Na_2SO_4 0.26 = Na 0.08478.

[1] In Morley and Muir's edition of Watts' "Dictionary," this formula is incorrectly quoted as $NaZnCy_3.5H_2O$.

[2] *Pogg. Ann.*, **42**, 112 (1837).

Whence the percentage is:

	Observed by Rammelsberg.		Calculated for $NaZnCy_3$ by Rammelsberg.	Recalculated for $NaZnCy_3$.[1]
Zinc	38.393	37.391	38.65	39.26
Sodium	14.951	14.624	13.938	13.84
Cyanogen	not estimated		47.422	46.9
Cyanogen by difference	(46.656)	(47.985)	.....	....
			100.01	100.0

Or a compound of 2 equivalents zinc cyanide with 1 equivalent of sodum cyanide, with which *5 equivalents of water* (*HO* in old atomic weights, *i. e.*, 2.5 molecules H_2O in new system) appear to be combined, which would make 21.23 per cent. water. *The discrepancy between the found and calculated results lies doubtless in a small admixture of sodium carbonate which was always mixed with the salts examined.*"

ATTEMPTS AT PREPARATION OF SODIUM ZINC CYANIDE.

I made several preliminary attempts to obtain this salt by dissolving precipitated zinc cyanide, first in solutions prepared from the "purest" sodium cyanide on the market, and then with a solution of caustic soda saturated with HCN. The only crystals obtained were filmy flakes, left when the solutions had been evaporated to a thick syrup by standing several weeks in desiccators over sulphuric acid.

Larger quantities of a stronger solution were then prepared but these refused to crystallize at all until some of the flakes previously obtained were dropped in; this induced a slow deposition of similar leaf-like crystals, several grams of which were finally obtained, and dried by pressing between filter-paper. Analyses of these are given below as Samples A and B. On attempting to redissolve these in a little water, so as to recrystallize and purify them, they decomposed to some extent, an insoluble basic cyanide of zinc separating out in small quantity; the new solution could not be induced to crystallize. It was impossible to free them completely from the mother-liquor, which was so concentrated as to affect the analysis seriously.

Another solution was similarly prepared and allowed to stand over sulphuric acid for over a month without yielding any crystals; it was then left out of doors two days in severely cold weather, the temperature ranging from 0° to —35° C., when some large

[1] W. J. S.: F. W. Clarke's atomic weights.

tabular crystals were formed; these, however, turned out to consist chiefly of sodium carbonate with 56 per cent. of water, and further crops had a similar composition.

A larger quantity of sodium cyanide was obtained and similarly saturated with zinc cyanide, after removing all traces of carbon dioxide. After very long evaporation a number of octahedral crystals were found which yielded, by analysis, zinc, 27 per cent., cyanogen, 42.8 per cent., water, 1 per cent., proportions corresponding closely to those of K_2ZnCy_4, which they proved to be, resulting from a small amount of potassium found to have been present in the sodium cyanide used in this preparation.

In the meantime a number of experiments had been made which seemed to indicate the solution of zinc cyanide in practically equal amounts by equivalent quantities of potassium and sodium cyanide. These suggested the existence of the compound Na_2ZnCy_4 in solution and in fact proved it so far as dilute solutions are concerned.

The ratio of zinc to cyanogen in the mother-liquor, from the first crop of crystals of sodium zinc cyanide, also corresponds to the existence of Na_2ZnCy_4 in that concentrated solution. Although the sodium zinc cyanide crystals obtained and analyzed, both in this investigation and by Rammelsberg, were decidedly impure, still the atomic ratio of zinc to cyanogen is so nearly 1:3 as to make it almost certain that Rammelsberg's formula, $NaZnCy_3$, is correct. There must, however, remain some uncertainty as to the degree of hydration of this salt, as it very easily loses its water of crystallization. Rammelsberg stated that the water was expelled completely at 200° C. In my experiments it was found to lose all but 2 per cent. by drying over sulphuric acid *in vacuo* at about 20° C.; the greater portion of the water was lost at about 70° C., and there was only a trifling loss of weight when the material, dried at 110°, was heated to fusion.

The comparison given below of the composition calculated and found for the anhydrous compounds shows a considerable variation in different analyses, but a fair approximation to the atomic ratio Zn:3Cy.

	Percentage composition.							
	Water in crystals.	Anhydrous salt.			Atomic ratio.			
		Sodium.	Zinc.	Cyanogen.	Water.	Sodium.	Zinc.	Cyanogen.
Na_2ZnCy_4 calculated	....	21.3	30.3	48.3	...	2.0	1.0	4.0
$NaZnCy_3$ calculated	....	13.84	39.26	46.9	...	1.0	1.0	3.0
Rammelsberg crystals, No. 1	21.7	14.951	38.393	46.656	2.28	1.10	1.0	3.05
Rammelsberg crystals, No. 2	22.88	14.624	37.391	47.958	2.34	1.11	1.0	3.22
W. J. S. sample A, dried over H_2SO_4.	2.0	19.3	34.2	45.8	...	1.6	1.0	3.36
W. J. S. sample B, dried on filter-paper	26.0	...	33.8	42.57	2.41	..	1.0	3.16
W. J. S. sample C, second crop.....	23.6	...	35.5	42.4	2.4	..	1.0	3.0
Mother-liquor	...	...	...	...	..	..	1.0	4.0

The mother-liquor from crystals in samples A and B was of a syrupy consistency and had a specific gravity of about 1.35. One cubic centimeter was found to contain zinc, 205 milligrams, cyanogen, 327 milligrams, corresponding almost exactly to the ratio Zn:4Cy.

If the sodium is calculated to correspond to the ratio 2Na:Zn we get 145 milligrams per cubic centimeter, or a total of 677 milligrams in 1 cc. or 1.35 grams of saturated solution, indicating that this salt, Na_2ZnCy_4, is soluble in its own weight of water.

METHOD OF CONDUCTING EXPERIMENTS ON THE ACTION OF POTASSIUM AND SODIUM HYDROXIDE AND CYANIDE UPON ZINC OXIDE AND CYANIDE.

The zinc cyanide was obtained in the form of an emulsion; by shaking this up and removing it with a pipette it was possible to gauge the quantity taken to within about 1 to 1.5 per cent., the material having been previously analyzed and being kept in a stoppered bottle. The zinc oxide was weighed out in most cases. The alkaline cyanide and hydroxide were kept in the form of fifth-normal solutions—double the strength intended for the experiments; except in preliminary experiments, the carbonate present was removed by addition of lime. Any slight excess of alkali in the cyanide solutions, due to hydroxide, was usually neutralized by the addition of standard sulphuric acid, the alkaline sulphate thus formed not interfering with the results.

In any series of experiments a number of graduated flasks were taken, and with a pipette of half their capacity they were half-filled with the fifth-normal solution of cyanide or hydroxide of potassium or of sodium. Water was then added to partly fill the remaining half of the flask, then the zinc oxide was added, or the zinc cyanide run in from a pipette in suitable amount; then water was added to fill the vessel to the mark (or slightly above the mark when the solid was added in large excess); the contents were thoroughly shaken, and allowed to stand with occasional shaking for some hours or days, either in the cold or with occasional heating. The contents were finally allowed to settle, and aliquot portions of the clear solution were removed with a pipette for analysis; zinc and cyanogen alone were determined, as it had been found that no alkali-metal was removed from the solution. In some instances the solutions were filtered off, in order to allow of examining the precipitates.

In the analyses the volumetric solutions were adjusted to some multiple of normal strength, and the weights of alkali-metal, zinc, or cyanogen, were not calculated but are stated as so many atoms, molecules, or equivalents per 100 cc. of solvent used, the solvent being decinormal in every case. One "atom," "equivalent," etc., as thus used, means the corresponding weight expressed in tenths of milligrams. In the tables, therefore, one can at once read, from the experimental data, the number of atoms of zinc, for instance, which passed into solution in a particular experiment, by the action of 100 molecules of alkaline cyanide or hydroxide.

SOLVENT ACTION ON GOLD OF SOLUTIONS OF POTASSIUM ZINC CYANIDE.

This is less than that of a solution of simple potassium cyanide containing the same amount, or one-half the amount, of cyanogen in equal volumes.

It is increased by addition of caustic alkali, other conditions remaining the same, and the increase is greatest in those solutions to which oxygen has the freest access.

The considerable increase in solvent power observed when caustic potash is added (always providing that oxygen is accessible), *coupled with the superior effect of free potassium cyanide, is good evidence that some free potassium cyanide is formed upon such addition,* and therefore that in dilute solutions *potassium zinc*

cyanide is partially decomposed by caustic alkali, with formation of simple alkaline cyanide, in accordance with the principles of chemical equilibrium between substances in solution.

ACTION OF DILUTE SOLUTIONS OF ALKALINE HYDROXIDES ON ZINC OXIDE.

This must be considered in connection with the side-reactions involved in the solution of zinc oxide in alkaline cyanides, or of zinc cyanide in alkaline hydroxide solutions, as will be shown later.

Prescott and Wilson[1] have shown that 8 molecules of potassium hydroxide, in a solution of *normal* strength, are necessary to precipitate and redissolve 1 molecule of zinc chloride or other zinc salt, and that 7 molecules of sodium hydroxide produce the same effect. Therefore 6 molecules of potassium hydroxide, or 5 of sodium hydroxide, are the least quantities which, in a normal solution, can dissolve freshly precipitated zinc hydroxide. The solutions must then contain: $K_2ZnO_2 + 4KOH$, or $Na_2ZnO_2 + 3NaOH$.

Heating or great dilution decomposed or dissociated these compounds, precipitating zinc oxide, but by cautious addition of acid all the excess of alkali could be neutralized, and alkaline zincate left.

In a more dilute, such as a decinormal, solution I have found the amount of zinc oxide dissolved per unit of alkali very much smaller, especially when a dry oxide is used, but that by careful neutralization the zincate may be left in solution if a very slight amount of free alkali is allowed to remain. The solution, however, is always precipitated on heating unless a considerable excess of free alkali is present.

DECINORMAL SOLUTIONS OF ALKALINE HYDROXIDES WITH ZINC OXIDE.

On leaving an excess of dry, finely divided, zinc oxide in contact with solutions of sodium and potassium hydroxides, both of tenth-normal strength, for several days, during which time they were frequently agitated, the amounts found in solution were as follows:

[1] This Journal, **2**, 27.

Potassium hydroxide, decinormal solution :

(1) Cold : 100 molecules potassium hydroxide dissolved 2.1 molecules zinc oxide.

(2) Cold : 100 molecules potassium hydroxide dissolved 2.7 molecules zinc oxide.

(3) Heated gently : 100 molecules potassium hydroxide dissolved 2.5 molecules zinc oxide.

Sodium hydroxide, decinormal solution :

(1) Cold : 100 molecules sodium hydroxide dissolved 4.5 molecules zinc oxide.

(2) Warmed : 100 molecules sodium hydroxide dissolved 8.3 molecules zinc oxide.

On boiling, either of the above solutions, a slight precipitate was thrown down.

The only importance of these last experimental results is to show how little tendency there is for the alkaline zincates to form in these dilute solutions, and how easily they are decomposed.

ACTION OF DILUTE (DECINORMAL) SOLUTIONS OF POTASSIUM CYANIDE UPON ZINC CYANIDE.

The results are given in Table I. In Nos. 1 to 4 the potassium cyanide contained some sodium cyanide and a little carbonate; the zinc cyanide was also basic. In Nos. 5 to 9 the zinc cyanide was almost exactly normal, but in 5 to 8 it had been kept several days and may have commenced to decompose with the formation of ammonia compounds.

ACTION OF A DILUTE (DECINORMAL) SOLUTION OF SODIUM CYANIDE UPON ZINC CYANIDE.

The sodium cyanide used contained a little free alkali, but only traces of other impurities. The zinc cyanide was almost normal and recently prepared: 5 cc. of the emulsion contained approximately 19 mol. $ZnCy_2$ + 1 mol. ZnO.

The ratio of zinc to cyanogen in the saturated solutions closely approximates 1 atom to 4. The solution appears to have followed very closely the reaction corresponding to $4NaCy + ZnCy_2 = Na_2ZnCy_4$, and it is, therefore, probable that the salt Na_2ZnCy_4, analogous to the corresponding potassium compound, is formed and exists in these dilute solutions. Increasing the proportion of zinc cyanide beyond that indicated in the equation has no appreciable effect, the excess remaining practically unacted upon.

TABLE I.—$KCN + Zn(CN)_2$.

Experiment No.	1.	2.	3.	4.	5.	6.	7.	8.	9.
Materials:	Commercial "98 per cent." potassium cyanide				Merck's purest potassium cyanide				
	Basic zinc		cyanide			Pure	zinc	cyanide	
Solvent contained in 100 cc.:									
Equivalents Cy	100	100	100	100	100	100	100	100	100
Atoms K(+Na in 1-4)	108.2	108.2	108.2	108.2	100	100	100	100	100
Zinc cyanide used:	Excess	Excess	Slight excess	Large excess	25 mol.	50 mol.	100 mol.	200 mol.	Large excess.
Treatment:	Cold	Heated occasionally	Cold	Warmed occasionally	Cold	Cold	Cold	Cold	Cold
Hours of contact	48	48	170	170	120	120	120	120	48
Residue[1] or precipitate	Moderate	Moderate	Slight	Large	None	Slight	Moderate	Large	Large
Solution analysis: 100 cc. were found to contain:									
Equivalents Cy	211	210	200	197	140	201.0	212	218	202
Atoms Zn	61.0	59.8	53.7	53.2	26.0	50.1	55.5	56.0	50.2
Composition calculated: molecules per 100 cc.:									
K_2ZnCy_4	49.25	49.65	50.0	49.2	26.0	50.0	50.0	50.0	50.0
K_2ZnO_2	4.85	4.45	3.7	4.0	0	0	0	0	0
$ZnCy_2$ in excess of K_2ZnCy_4	7.0[2]	5.7[2]	0	0	0	0.1	5.5	6.0	0.2
	....	....	0.8 KOH	1.8 KOH	36 KCy	....	....	....	....
Cy not accounted for	....	....	....	....	....	0.8	1.0	6.0	1.6

[1] The composition of the precipitates was examined in the case of Nos. 7 and 8; there was found for each 100 cc. of solution obtained:
In No. 7, Zn 20 atoms, Cy 37 equivalents; = 18.5 $ZnCy_2$, 1.5 ZnO.
In No. 8, Zn 99.5 atoms, Cy 198 equivalents; = 99 $ZnCy_2$, 0.5 ZnO.
The amounts thus found do not account for all the zinc cyanide left undissolved, as only about two-thirds of the residues could be retained by filtration; they prove, however, that the composition of the undissolved portion was practically unaltered. *The reaction is undoubtedly* $4KCy + ZnCy_2 = K_2ZnCy_4$ *complicated slightly by impurities.* The excess of cyanogen and of zinc in some cases is probably due to small amounts of ammonium compounds developed in the zinc cyanide.

[2] In Nos. 1 and 2 the solutions were opalescent, a little zinc cyanide remaining in suspension.

TABLE II.—$NaCN + ZnCy_2$.

Experiment No.	1.	2.	3.
Solvent contained in 100 cc.:			
Equivalents Cy	100	100	100
Atoms Na	108.3	108.3	108.3
Zinc cyanide used :			
Cc. emulsion	5.0	15.0	25.0
Molecules $ZnCy_2$	19.0	57.0	95.0
Molecules ZnO	1.0	3.0	5.0
Hours of contact	24.0	120.0	120.0
Solution analysis, found in 100 cc.:			
Equivalents Cy	...	200.5	202.0
Atoms zinc	....	50.2	51.0
Residue	None	Moderate	Heavy
Residue analysis, per 100 cc. solution :			
Equivalents Cy	0	9.0	82.0
Atoms Zn	0	5.0	42.0
Composition calculated : molecules per 100 cc. of solution :			
In solution : Na_2ZnCy_4	20.0	50.1	50.5
Na_2ZnO_2	0.0	0.1	0.5
NaOH	10.3	8.1	6.3
NaCy in excess	58.0	0.0	0.0
In residue : $ZnCy_2$	0.0	4.5	41.0
ZnO	0.0	0.5	1.0

ACTION OF DILUTE (DECINORMAL) SOLUTIONS OF POTASSIUM CYANIDE UPON ZINC OXIDE.

In all but the first four experments, the results of which are given in Table III, the potassium cyanide solution was free from carbonate, and the small amount of free alkali found was carefully neutralized by addition of standard sulphuric acid. A residue was left in every case but that in No. 7 was excessively small. The residue was tested in several instances, and proved to be zinc oxide holding a mere trace of cyanogen.

Examining the results obtained with cold solutions it will be seen that they all correspond closely to the equation:

$$100KCy + 30ZnO + 20H_2O = 25K_2ZnCy_4 + 5K_2ZnO_2 + 40KOH$$

or, simplifying,

$$20KCy + 6ZnO + 4H_2O = 5K_2ZnCy_4 + K_2ZnO_2.8KOH;$$

that is to say, that the potassium cyanide is apparently completely converted into the double zinc potassium cyanide, with formation of potassium hydroxide, which dissolves a further portion of zinc oxide. After calculating all the cyanogen in solution to K_2ZnCy_4,

TABLE III.—KCN + ZnO.

Experiment No.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.
Materials	Comm'l "98%" KCN (+ NaCN). Dense finely powdered ZnO.				Merck C.P. KCN. Fresh $Zn(OH)_2$.		Merck's C.P. KCN. Baker & Adamson's C.P. ZnO, very finely divided.					"V. H. P. KCN," nearly pure. Merck's C.P. ZnO, very finely divided.				
Solvent contained in 100 cc.:																
Equivalents Cy	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Atoms K	108.2	108.2	108.2	108.2	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide added	Slight excess	Large excess	Slight excess	Large excess	Excess	Excess	20 mol.	35 mol.	70 mol.	70 mol.	70 mol.	48 mol.	50 mol.	100 mol.	48 mol.	100 mol.
Treatment	Cold	Cold	Boiled occa'ly	Boiled occa'ly	Cold	Heated occas'ly	Cold	Cold	Cold	Heated occasionally.		Heated	Cold, often shaken.		Heated gently continuously.	
Hours contact before testing	48	48	48	48	48	48	48	120	120	48	48	36	36	36	36	36
Solution analysis; 100 cc. were found to contain:																
Equivalents Cy	100.5	100.0	100.2	100.0	(100)[1]	(100)[1]	(100)[1]	99.8	100.1	100	(100)[1]	98.0	99.2	100.0	94.0[2]	93.0[2]
Atoms zinc	27.6	31.6	28.2	29.5	32.0	33.1	20.0	30.4	30.6	28.5	28.2	29.8	29.7	29.7	27.9	27.6
Composition calculated; molecules per 100 cc.:																
K_2ZnCy_4	25.1	25.0	25.05	25.0	25.0	25.0	20.0	24.95	25.02	25.0	25.0	24.5	24.8	25.0	23.5	23.2
K_2ZnO_2	2.5	6.6	3.2	4.5	7.0	8.1	0.0	5.45	5.58	3.5	3.2	5.3	4.9	4.7	4.4	4.4
KOH	53.0	45.0	51.7	48.8	36.0	33.8	40	39.2	38.8	43.0	43.4	40.4	40.6	40.6	44.2	44.8
KCy	0.0	0.0	0.0	0.0	0.0	0.0	20	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

[1] Assumed.

[2] Loss of cyanogen due probably to continuous heating.

the residual potassium and zinc correspond very closely to the composition $K_2ZnO_2.8KOH$, which agrees with the finding of Prescott and Wilson,[1] that 8 molecules of potash are necessary in a *normal* solution to precipitate and redissolve 1 molecule of zinc oxide, corresponding to $K_2ZnO_2.4KOH$ in a solution of *normal* strength, while a larger excess of alkali is required for solution in a weaker solution, such as the decinormal solution used in these experiments.

ACTION OF A DILUTE (DECINORMAL) SOLUTION OF SODIUM CYANIDE UPON ZINC OXIDE.

The sodium cyanide used was of the very highest purity, it was freed from carbonates by lime-water, and the slight amount of free alkali remaining was neutralized by standard sulphuric acid. The zinc oxide was Merck's chemically pure, prepared by a dry process, and was very finely divided. Contact was maintained for about thirty-six hours, during the first twenty-four of which the mixtures were frequently shaken.

TABLE IV.—NaCN + ZnO.

Experiment No.	1.	2.	3.	4.	5.	6.
Solvent contained in 100 cc.:						
Equivalents Cy	100	100	100	100	100	100
Atoms Na	100	100	100	100	100	100
Zinc oxide added in molecules	25	50	75	100	50	100
Treatment	Cold	Cold	Cold	Cold	Warmed	Warmed
Found in resulting solution per 100 cc.:						
Equivalents Cy	100.5	100.0	..	..	100.0	99.0
Atoms zinc	23.2	30.0	30.0	30.3	28.5	28.8

A residue was left in every case but No. 1, in which all but a mere trace of the oxide had dissolved.

From the very close agreement of the ratio between the zinc found in solution and the solvent taken, with the similar ratio observed in the case of potassium cyanide solutions acting on zinc oxide, it is evident that the reactions in the two cases are practically identical. The calculation of the molecular composition of the resulting solution has, therefore, been omitted.

The ratio evidently corresponds to the reaction between 20 molecules NaCy and 6 molecules ZnO, and the equation corresponding may be stated:

$$20NaCy + 6ZnO + 4H_2O = 5Na_2ZnCy_4 + Na_2ZnO_2.8NaOH.$$

[1] This Journal, **2**, 27.

ACTION OF COLD DILUTE (DECINORMAL) SOLUTIONS OF POTASSIUM HYDROXIDE UPON ZINC CYANIDE.[1]

The potassium hydroxide used was freed from carbonate, and the zinc cyanide was nearly normal and recently prepared.

From the experimental results which are tabulated in Table V it appears that zinc cyanide is dissolved readily and permanently by a decinormal solution of potassium hydroxide, up to the point corresponding to the proportion $2KOH + ZnCy_2$; further additions dissolve less readily up to the point of saturation, which occurs when the number of molecules of zinc cyanide added approaches that of the potassium hydroxide; any zinc cyanide in excess of the proportion $ZnCy_2 + KOH$ is unacted upon. If the solution has been thus saturated with zinc cyanide, or if the amount dissolved exceeds the proportion 1 molecule $ZnCy_2 + 2$ molecules KOH, then a precipitate soon begins to form and continues to fall out for some time, or until equilibrium is reached; this precipitate consists of pure zinc oxide, which is deposited in a finely divided form and adheres closely to the sides of the containing vessel.

If the mixture is warmed, the precipitation is hastened and equilibrium is soon reached. In any case, the *final* solution approaches the composition K_2ZnCy_4, but in cases where the zinc cyanide is but slightly in excess of the proportion $ZnCy_2 + 2KOH$, an appreciable amount of potassium zincate seems to remain in solution unless heat is applied, when it soon decomposes with deposition of zinc oxide.

The complete reaction, *when zinc cyanide is in excess and after equilibrium has been attained,* approaches that represented by the equation $2KOH + 2ZnCy_2 = K_2ZnCy_4 + ZnO + H_2O$. If, however, the potassium hydroxide is in excess, the reaction appears to be $4KOH + 2ZnCy_2 = K_2ZnCy_4 + K_2ZnO_2 + 2H_2O$. If the proportion of molecules of hydroxide to zinc cyanide lies between 1 : 1 and 2 : 1, there appears to be a mixed reaction, involving both of the above equations.

The composition assigned by calculation to the various solutions examined, as regards proportion of potassium zinc cyanide and potassium zincate, is verified by the behavior of these solutions on heating, those in which the larger proportions of zincate are indicated depositing the heavier precipitates of zinc oxide.

[1] See Curves *A* and *B*.

TABLE V.—KOH + $ZnCy_2$.

Experiment No.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Molecules KOH in 100 cc. of solvent	100	100	100	100	100	100	100	100	100	100
Molecules $ZnCy_2$ added	13	26	42	52	52	78	100	100	125	250
Effect	Dissolved completely						Dissolved except tr.	Dissolved except tr.	Some insol. residue	Much insol. residue
On standing	No pp.	No pp.	12 hrs. very slight flocc't pp.	2 hrs., slight pp., pulverulent, forms slowly.	2 hrs. slight pp., forms slowly.	4 hrs. heavy pp., pulv't and flocc't.	1 hr. heavy pp., pulv't and flocc't.	1 hr. heavy pp., pulv't and flocc't.	5 minutes, heavy pp., pulv't, forms rapidly.	5 minutes, heavy pp., pulv't, forms rapidly.
Effect of boiling a portion of clear supernatant solution[1]	Slight pp.	Moderate pp.	Heavy pp.	Heavy pp.	Heavy pp.	Moderate pp.	Slight pp. in 2 min.	Slight pp. in 5 min.	No. pp.	No. pp.
Solution analysis ; 100 cc. were found to contain :										
Equivalents Cy	25.6	52.0	81.2	100.5	104.2	157.1	192.4	197.0	205.5	207.0
Atoms Zn	12.95	26.2	38.9	40.04	38.1	47.0	54.1	55.8	57.6	59.0
Residue and precipitates found per 100 cc. of solution :										
Equivalents Cy	0	0	1.0	1.0	1.0	2.0	15.0	15.0	45.0	290.0
Atoms Zn	0	0	8.66	13.0	16.6	20.6	46.4	52.0	64.3	190.0
Composition calculated : molecules per 100 cc. of solution ; in solution :										
K_2ZnCy_4	6.4	13.0	20.3	25.13	26.05	39.3	46.05	46.35	47.6	47.25
K_2ZnO_2	6.55	13.2	18.6	14.9	12.05	7.7	3.95	3.65	2.4	2.75
KOH free	74.1	43.6	22.2	19.92	23.8	6.0	0	0	0	0
$ZnCy_2$	0	0	0	0	0	0	4.1	5.8	7.6	9.0
In residue and precipitate :										
$ZnCy_2$	0	0	0.5	0.5	0.5	1.0	7.5	7.5	22.5	145.0
ZnO	0	0	8.16	12.5	16.1	19.6	39.0	44.5	41.8	45.0

[1] In one case (No. 8) the solution was examined after heating and found to contain, per 100 cc., 196 equivalents Cy, 50.1 atoms Zn, corresponding to a composition of 49 molecules K_2ZnCy_4, and 1 molecule K_2ZnO_2. The solution had the characteristic sweet taste of potassium zinc cyanide, slightly modified by the free alkali present.

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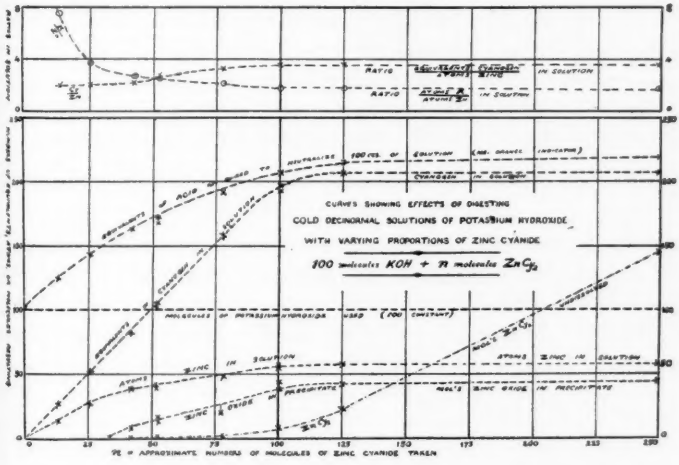
The reaction taking place when the larger proportion of zinc cyanide passes into unstable solution—1 molecule of zinc cyanide for 1 molecule of hydroxide of either potassium or sodium as shown in tables V and VI—may possibly be accounted for by the formation (in the latter case) of the unstable compounds $NaZnCy_3$[1] and $Na_2Zn_2O_3$,[2] and possibly $KZnCy_3$ and $K_2Zn_2O_3$,[3] in the former,

$$6NaOH + 6ZnCy_2 = 4NaZnCy_3 + Na_2Zn_2O_3 + 3H_2O,$$

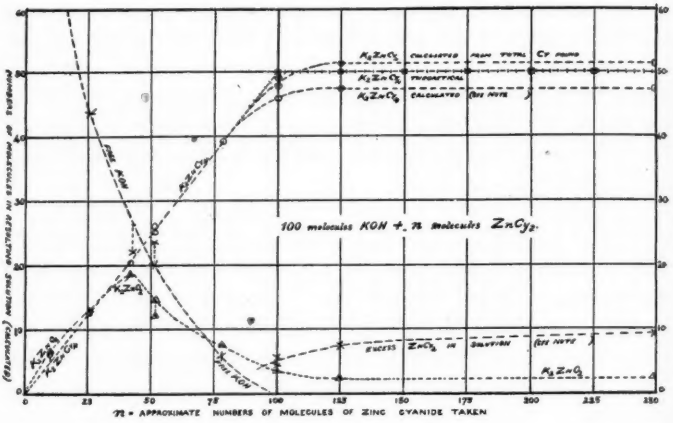
the latter compounds splitting up to form $3Na_2ZnCy_4 + 3ZnO$. This is suggested as a probable explanation of the instability of the solutions thus formed, the compounds $K_2Zn_2O_3$ and $Na_2Zn_2O_3,H_2O$ (or $NaHZnO_2$) being stated by their discoverers to be decomposed by water, while from the experiments already described it appears that $NaZnCy_3$ is obtained only in concentrated solutions.

The curves appended show more clearly the variation in composition found with addition of varying proportions of zinc cyanide and constant quantities of potassium hydroxide. Curve *A* indicates the results directly obtained by analysis of solutions and residues, while Curve *B* shows the molecular proportions of double cyanide, zincate, and other products calculated therefrom.


CURVES SHOWING EFFECTS OF DIGESTING
COLD DECINORMAL SOLUTIONS OF POTASSIUM HYDROXIDE
WITH VARYING PROPORTIONS OF ZINC CYANIDE
100 molecules KOH + N molecules ZnCy2
PERCENTAGE
ZINC IN SOLUTION
ZINC AS OXIDE
ZINC IN PRECIPITATE
N = APPROXIMATE NUMBER OF MOLECULES OF ZINC CYANIDE TAKEN

Curve *A*. Fig. 1.

[1] Rammelsberg: *Pogg. Ann.*,
[2] Comey and Jackson: *Am. Chem. J.*, **11**, 145.
[3] Fremy: *Compt. rend.*, **15**, 116.



Curve *B*. Fig. 2.

The fact that in some cases, especially when the proportion of zinc cyanide was very large, the amounts of zinc and of cyanogen finally found in the solution were somewhat in excess of those corresponding to the formation of K_2ZnCy_4, may be explained either by the dissolving of some $ZnCy_2$ as such, or by its forming a certain proportion of $KZnCy_3$ which remains undecomposed, but the most probable explanation is the formation of a small amount of ammonia in the zinc cyanide, either before or during the experiments, 3 molecules of ammonia having been found to dissolve 1 molecule of zinc cyanide, when applied in dilute solution.

ACTION OF DILUTE (DECINORMAL) SOLUTIONS OF SODIUM HYDROXIDE UPON ZINC CYANIDE.

The general effects on mixing zinc cyanide with sodium hydroxide were similar to those with potassium hydroxide. The zinc cyanide dissolved readily on the first additions, then more slowly until the number of molecules of zinc cyanide dissolved approached that of the sodium hydroxide, when the solution became saturated: on standing, such a saturated solution deposited about half the dissolved zinc as oxide. In the final solution, however, the proportion of cyanogen present to sodium hydroxide taken is smaller than is the case with an equivalent amount of potassium hydroxide, when an excess of zinc cyanide is used, *viz.*, about 180

TABLE VI.—$NaOH + ZnCy_2$.

Experiment No.	1.	2.	3.	4.	5.	6.	7.
Materials:	Caustic soda with a little carbonate Basic zinc cyanide				Pure caustic soda Pure zinc cyanide		
Solvent contained in 100 cc.							
NaOH in molecules	100	100	100	100	100	100	100
Zinc cyanide added	Slight deficiency	Slight excess	Large excess	Large excess	82 mols.	102 mols.	136 mols.
Treatment	Cold	Cold	Cold	Warmed occasionally	Cold	Cold	Cold
Effect	Dissolved completely	Dissolved except trace	Considerable residue	Much residue	Dissolved completely	Dissolved except trace	Much residue
On standing	Slight pp.	Pp. slowly formed	Heavy pp.	Heavy pp.	Pp. slowly formed	Heavy pp.	Heavy pp.
Cyanogen in pp. or residue	None	Trace	Much	....	Trace	....	Much
Effect of boiling a portion of clear supernatant solution	Pp. finally very heavy	Slight pp.	Slight pp. after time	Very slight pp.	Slight pp.	Slight pp.	Very slight pp.
Solution analysis: 100 cc. were found to contain:							
Equivalents Cy	137.0	177.0	183.0	166.0	165.0	181.0	184.0
Atoms Zn	44.0	50.0	53.8	41.5	48.6	49.6	51.0
Composition calculated: molecules per 100 cc. solution:							
Na_2ZnCy_4	34.25	44.25	43.85	41.5	41.25	45.25	45.5
Na_2ZnO_2	9.75	5.75	6.15	0.0	7.35	4.35	4.5
NaOH free	12.0	0.0	0.0	17.0	2.8	0.8	0.0
$ZnCy_2$ in excess	0.0	0.0	3.8	0.0	0.0	0.0	1.0

equivalents cyanogen to 100 of soda, as against about 200 cyanogen to 100 of potash.

The extent of precipitation upon heating the clear solutions agrees in a general way with the proportion of zincate calculated when the cyanogen is reckoned as Na_2ZnCy_4, but not when it is reckoned as $NaZnCy_3$.

It will be noted that the values for Na_2ZnCy_4, etc., in Nos. 5, 6, and 7 fit within 1 or 2 units of those plotted in Curve *B* for K_2ZnCy_4 on the parallel experiments with KOH. Compare also Table V.

After heating, the solution was examined only in the case of No. 6, the analysis of which showed 181 equivalents cyanogen and 46 atoms zinc, corresponding to 45.25 molecules Na_2ZnCy_4, as before, 0.75 molecule Na_2ZnO_2, and 8 molecules NaOH, which would indicate the stability of the compound Na_2ZnCy_4, confirmed also by the results of No. 4, the unstable sodium zincate being almost completely decomposed by the heating.

The length of time of contact in experiments 1 to 4 was not recorded but was at least three to four days; in Nos. 5 to 7 it was forty-eight hours.

ACTION OF SODIUM CARBONATE SOLUTION ON ZINC CYANIDE.

A solution of sodium carbonate of known strength and volume was mixed with a considerable quantity of basic zinc cyanide. Two such mixtures were made, each was placed in a graduated vessel and water added till the total volume in each was such that 100 cc. contained 20 milligram-molecules (200 mols) Na_2CO_3. These mixtures were left for forty-eight hours. No. 1 was kept cold, but shaken at intervals. No. 2 was heated to boiling-point for about two minutes at the start, and again after twenty-four hours, and also shaken occasionally. After forty-eight hours zinc and cyanogen were estimated in the clear solutions.

The character of the semi-transparent, gelatinous, zinc cyanide changed soon after being introduced, very rapidly on warming, becoming dead-white and bulky,—resembling zinc carbonate, which was probably formed in part. The residue settled slowly but was *very easily filtered off*. A little gas was given off from No. 2 after heating.

	No. 1.	No. 2.
Treatment (48 hours)	Cold.	Heated.
100 cc. contain finally:		
Atoms Na (from solvent)	400.0	400.0
Atoms Zn (dissolved)	49.8	72.0
Equivalents Cy (dissolved)	144.0	236.0
Ratio Cy/Zn	2.9	3.3
Ratio Na/Zn	8.0	5.5
Ratio Cy/Na	0.36	0.59

There seems to have been no complete reaction. According as Na_2ZnCy_4 or $NaZnCy_3$ were formed (see sodium zinc cyanide above), one would expect a reaction such as illustrated by the equation

$$Na_2CO_3 + 2ZnCy_2 = Na_2ZnCy_4 + ZnCO_3$$

or

$$Na_2CO_3 + 3ZnCy_2 = 2NaZnCy_3 + ZnCO_3,$$

as zinc carbonate is evidently one of the products. The latter reaction (forming $NaZnCy_3$) is apparently suggested by the ratio of the zinc and cyanogen, but the ratios of both zinc and cyanogen to sodium are so small as to make it certain that much of the sodium carbonate remained undecomposed.

The resulting clear solution acted as a solvent for gold.

SUMMARY OF RESULTS.

When an alkaline solution, containing potassium, zinc and cyanogen, is concentrated, potassium zinc cyanide (K_2ZnCy_4) readily crystallizes out and can be easily obtained in a state of considerable purity. This salt is also formed in solution when potassium cyanide acts on zinc cyanide or zinc oxide, or when potassium hydroxide acts upon an excess of zinc cyanide, as, when equilibrium is attained, and any zincate formed is decomposed by heating, the atomic ratio of zinc to cyanogen in the solution is almost exactly 1:4.

A sodium cyanide solution, saturated with zinc cyanide and concentrated, crystallizes with extreme difficulty to form hydrated crystals of sodium zinc cyanide ($NaZnCy_3$) which it seems impossible to obtain pure, and which decompose to some extent on addition of water, precipitating basic zinc cyanide. This salt does not appear to exist in the solution, as the mother-liquor contains zinc and cyanogen in approximately the ratio of 1:4. Also when dilute solutions of sodium cyanide act on zinc cyanide or oxide, or sodium hydroxide on an excess of zinc cyanide, the atomic ratio

of zinc to cyanogen in the resulting solution is approximately 1 : 4, so that the compound Na_2ZnCy_4 is contained both in dilute and concentrated solutions.

The hydroxides of potassium or sodium, in decinormal solution, dissolve very little zinc oxide when agitated with it; the zincate formed is largely decomposed on boiling, depositing zinc oxide, even in the presence of a large proportion of alkali.

Potassium cyanide, in dilute solution, dissolves zinc cyanide in accordance with the equation

$$2KCy + ZnCy_2 = K_2ZnCy_4,$$

forming a stable solution, little affected by long boiling or by the presence of carbonic acid. In dilute solutions, sodium cyanide appears to follow a similar reaction with zinc cyanide, $2NaCy + ZnCy_2 = Na_2ZnCy_4$, but on concentrating the solutions the formation of the crystals of a different compound indicates that the reaction $NaCy + ZnCy_2 = NaZnCy_3$ takes place under certain conditions.

Potassium cyanide, in decinormal solution, dissolves small proportions of zinc oxide completely. When the zinc oxide is present in excess, it is dissolved in the proportion of 3 molecules of zinc oxide for 10 molecules of potassium cyanide, agreeing with the equation

$$20KCy + 6ZnO + 4H_2O = 5K_2ZnCy_4 + K_2ZnO_2.8KOH,$$

which may be explained as taking place in two steps,

$$4KCy + ZnO + H_2O = K_2ZnCy_4 + 2KOH,$$

the potassium hydroxide further reacting,

$$10KOH + ZnO = K_2ZnO_2.8KOH + H_2O.$$

On boiling the solution of mixed double cyanide and zincate, the latter is partially decomposed with precipitation of zinc oxide.

With dilute solutions of sodium cyanide, the effects upon zinc cyanide are precisely similar to those observed with potassium cyanide under similar conditions.

Dilute solutions of potassium hydroxide dissolve zinc cyanide. If the zinc cyanide is in less than the proportion corresponding to $ZnCy_2 + 2KOH$, it is dissolved completely and permanently:

$$4KOH + 2ZnCy_2 = K_2ZnCy_4 + K_2ZnO_2 + 2H_2O,$$

although upon heating the solution most of the zincate is decomposed with precipitation of zinc oxide, leaving free alkali in solution. Zinc cyanide is also completely dissolved in proportions

up to that of $ZnCy_2 + KOH$, but a precipitate of zinc oxide begins shortly to fall out. Any zinc cyanide in excess of the last proportion stated is unaffected by the solvent.

When the zinc cyanide corresponds to, or is in excess of, the proportion of 1 molecule to 1 of hydroxide, it is dissolved in that proportion, but one-half of the zinc separates out as oxide, the separation beginning soon after solution, and going on slowly. The complete reaction, with an excess of zinc cyanide, and after equilibrium has been attained by the separation of oxide, agrees with the equation

$$2KOH + 2ZnCy_2 = K_2ZnCy_4 + ZnO + H_2O.$$

When a very large excess of zinc cyanide had been added, the zinc and cyanogen in solution sometimes slightly exceeded the proportions indicated by this equation, probably owing to the development of a little ammonia by the decomposition of zinc cyanide before or during the experiment.

With sodium hydroxide and zinc cyanide the general effects observed were precisely similar to those just described, but rather less of the zinc cyanide was dissolved in the cold than would correspond to a reaction exactly parallel to that with potassium hydroxide. On heating the solution, however, a little more zinc oxide separated, and the proportion of zinc and cyanogen in solution then agreed closely with the formula Na_2ZnCy_4.

The solution of so large a proportion of zinc cyanide by the caustic alkalies (1 molecule for each molecule of hydroxide), when first brought together, is somewhat difficult of explanation. It seems most probable that some compounds, richer in zinc than the salts Na_2ZnCy_4 and Na_2ZnO_2, are temporarily formed, *e. g.*, by some such reaction as the following,

$$6NaOH + 6ZnCy_2 = 4NaZnCy_3 + Na_2Zn_2O_3 + 3H_2O,$$

which, being unstable in dilute solution, soon break up;

$$4NaZnCy_3 + Na_2Zn_2O_3 = 3Na_2ZnCy_4 + 3ZnO,$$

similar reactions taking place with the potassium compounds.

Although the potassium zinc cyanide, K_2ZnCy_4, is exceedingly stable at very varying temperatures and degrees of dilution, and crystallizes readily out of impure and strongly alkaline solutions, still the reaction

$$K_2ZnCy_4 + 2KOH = K_2ZnO_2 + 4KCy + H_2O,$$

or a similar one, appears to take place, probably to a limited ex-

tent, when the double cyanide is mixed with potassium hydroxide in solution, for the gold-dissolving power of a double cyanide solution is considerably increased by addition of caustic alkali, the increment of solvent power decreasing for successive equal additions of alkali.

Several other reactions have been suggested as taking place between some of the substances investigated, but no experimental verification has been found for those investigated; for instance, the equation $K_2ZnCy_4 + 2KOH = Zn(OH)_2 + 4KCy$ is contrary to all observed facts.

THE ALKALOIDS OF ADLUMIA CIRRHOSA.

By J. O. Schlotterbeck and H. C. Watkins.

Received March 31, 1903.

[SECOND PAPER.]

In a previous paper,[1] "Adlumia Cirrhosa, a New Protopine-bearing Plant," the preliminary experiments upon the root of the first year's plant of this biennial were reported. Of the dried root only about 100 grams were available and it was treated as follows: It was first moistened with dilute ammonia water for the purpose of liberating the alkaloids from their combinations with acids. To avoid any possible change in the nature of the constituents, the powder was dried at room temperature by spreading out in thin layers in a room in which there was good circulation of air. The drug was now exhausted with chloroform in a Soxhlet apparatus since most free alkaloids are easily soluble in this solvent. The chloroform was recovered from the solution by distillation and the stiff, waxy residue then repeatedly digested with hot, very dilute acetic acid until all alkaloidal matter had been extracted. The combined acid aqueous extracts were concentrated, cooled, filtered and precipitated with ammonia water, being careful to avoid a great excess. The curdy precipitate was thoroughly washed on a filter, redissolved in dilute acetic acid, placed in a separator, made alkaline with ammonia and shaken out with ether. Solution of the alkaloid was almost instantaneous but only temporary. The ethereal liquid was passed through a tuft of cotton into a wide-mouthed flask and set aside. In a very short time

[1] *Am. Chem. J.*, **24**, 249.

crystals began to separate and in the course of two hours most of the alkaloid had crystallized out. This alkaloid upon purification was found to be protopine, and at the time it was thought that this was the only alkaloid present in the root.

Wishing to continue the chemical study of this interesting and widely known plant, an endeavor was made to secure it in large quantities. Although it is claimed that it grows wild in wet woods from New England to Michigan and eastern Kansas southward, it was impossible to obtain the plant from botanic druggists, and collectors could not be found to gather it. It was then decided to grow it ourselves. The small, shiny black seeds were obtained without difficulty from seedsmen and sowed as directed, in spring. Not a single seed germinated that year. Not desiring to postpone the work for a year, growing plants were solicited from the citizens of Ann Arbor who grow it quite generally about porches and doorsteps. About 150 of the first year's plants and sufficient of the second year's vine to make about 15 pounds when dry were kindly donated. The growing plants were transplanted to the experimental garden and the following year's crop reserved for further study. It has since been learned that the seeds are very slow in germinating and must be sown in a cool, moist soil.

Self-sown seeds do not germinate as a rule until June of the following year.

In the present study the entire plant of the second year's growth was employed, no attempt being made to separate root from stem or leaves. The finely ground drug was treated exactly as outlined above. About 30 grams of a dirty gray mass of alkaloids was obtained and after redissolving in dilute acetic acid, making alkaline with ammonia water and shaking out with ether, several different forms of crystals separated. They were isolated as far as possible mechanically, and each one purified by many recrystallizations. Five distinct alkaloids were isolated by fractional crystallization as follows:

ALKALOID I, PROTOPINE.

The identity of this alkaloid was established in the preliminary examination which has been reported. It has the composition $C_{20}H_{19}NO_5$ and melts at 204°-205° C.

ALKALOID II, β-HOMOCHELIDONINE.

This alkaloid crystallized in rather characteristic form, *viz.*, in beautiful clusters or rosettes of boat-shaped crystals with truncated ends. When purified, the crystals melted at 159° C. Sulphuric acid gives at once a rose-pink color which is intensified when the vapor of nitric acid is blown over it. Erdman's reagent colors it yellowish, then passing into beautiful violet.

Combustions gave the following results:

	Calculated for $C_{21}H_{23}NO_5$.	Found. I.	Found. II.
Carbon	68.27	68.66	68.6
Hydrogen	6.24	6.2	6.9
Nitrogen	3.8	3.8	3.76

ALKALOID III, ADLUMINE.

This alkaloid constituted the principal portion of the entire or total alkaloid. After purification it melted at 188° C. It crystallizes easily and in beautiful large crystals. A mixture of chloroform and alcohol constitutes the best crystallizing medium, from which large colorless, orthorhombic crystals can be obtained.

The following color tests were obtained:

Sulphuric acid.....Lemon-yellow.
Erdmann's reagent.....Olive-green to brown, then wine-red.
Nitric acid.....Lemon-yellow to orange.
Marquis' reagent.....Light yellow, changing to lavender.

A weighed quantity of desiccator-dried material lost no weight upon heating for several hours at 100° C. It therefore contains no water of crystallization. The material at hand permitted the following combustions for composition:

	Calculated for $C_{39}H_{39}NO_{12}$.	Calculated for $C_{39}H_{41}NO_{12}$.	Found. I.	Found. II.	Found. III.
Carbon	65.62	65.45	65.95	65.77	65.45
Hydrogen	5.46	5.74	5.75	5.64	5.59
Nitrogen	1.97	1.96	2.08	2.18	2.02
Oxygen	26.95	26.85	26.22	26.41	26.94

From the above results alone it is impossible to determine, with certainty, whether the formula is $C_{39}H_{39}NO_{12}$ or $C_{39}H_{41}NO_{12}$, the difference of two atoms of hydrogen being difficult to adjust because of the size of the molecule.

Platinum chloride does not precipitate the alkaloid from its solution. Gold chloride throws down a copious yellow, amorphous

precipitate, which can be crystallized by redissolving in hot water and allowing to cool. The crystals of the gold salt are deep orange-red in color, and contain no water of crystallization. During crystallization, a part of the gold is reduced. Incineration of the gold salt did not furnish concordant results, as we were probably dealing with a mixture of reduced gold and gold salt. This reaction will be studied further when more material is available.

Determination of Methoxyls.—Of the pure alkaloid, 0.100 gram was treated according to the Zeissel method for the determination of methoxyls. An abundant precipitate of AgI was formed in the flask containing the $AgNO_3$ solution. This was transferred to a Gooch crucible thoroughly washed, dried and weighed. The weight of AgI (0.847 gram) is equivalent to 8.68 per cent. methoxyl calculated from the formula having the higher hydrogen content. This is exactly equal to two methoxyl groups.

Determination of Hydroxyls.—A small amount of the pure alkaloid was heated with acetic anhydride on the steam-bath for several hours and the solution then evaporated to dryness. The amber-colored residue was taken up with a little chloroform, alcohol added and set aside. Colorless crystals, which melted at 177° C. when purified, separated quite rapidly.

Of this compound, 0.1412 gram was saponified by boiling with freshly prepared $Mg(OH)_2$ under a reflux condenser for two hours. Upon cooling, the liquid was filtered, the precipitate thoroughly washed, all the washings combined and concentrated and the magnesia determined as $Mg_2P_2O_7$. The weight obtained was 0.0202 $Mg_2P_2O_7$ which is equivalent to 5.54 per cent. of the acetic radical. Theory requires 5.68 per cent. for one acetyl group based on the formula with higher molecular weight.

The compound is then written $C_{37}H_{34}(OH)(OCH_3)_2NO_9$.

Finally, this alkaloid, which we have named adlumine because it seems not to have been known before, rotates the plane of polarized light $(\alpha)_D = +39.88$.

ALKALOID IV, ADLUMIDINE.

This alkaloid crystallizes in small, almost colorless, square plates melting at 234° C. When perfectly pure it is colorless, but it is extremely difficult to remove the last traces of the yellow color which adheres to it. It appears to be also a new alkaloid and we have therefore named it adlumidine.

The quantity available was too small to permit of more than the following combustions:

	Calculated for $C_{30}H_{29}NO_9$.	Found. I.	II.	III.
Carbon	65.6	65.69	....	65.45
Hydrogen	5.3	5.6	5.1	5.2
Nitrogen	2.54	2.6	....	2.63
Oxygen	26.5	26.11	....	26.72

The color reactions are striking.

Sulphuric acid.....Bright red, changing to olive-brown, then pink.
Erdmann's reagent....Brick-red, changing to shades of green, to brown.
Nitric acid.....Orange to light yellow.
Marquis' reagent.....Bright red to dark brown, then purple-violet.

ALKALOID V, UNNAMED.

This alkaloid was found in such small quantity that only the melting-point 176°-177° C. and the color reactions could be determined.

Sulphuric acid.....Light yellow.
Erdmann's reagent.....Dirty olive, brown, wine-red.
Nitric acid.....Light yellow.
Marquis' reagent.....No color.

ORGANIC ACIDS.

The dregs left after removing the alkaloids with chloroform were percolated with boiling water and the percolate concentrated to a small volume. Upon cooling, a crystalline sediment accumulated in the bottom of the dish. This dark-colored deposit was collected on a Büchner filter and thoroughly washed with cold water. There was left a grayish granular mass of salts of ammonia and calcium. This mass was dissolved in hot water with the aid of a little acetic acid, and then precipitated with a solution of lead subacetate. This precipitate was collected and rapidly washed with cold water by the aid of suction, then suspended in water and decomposed with hydrogen sulphide, the lead sulphide removed by filtration and the filtrate evaporated to dryness. This was boiled with alcohol and filtered. From the filtrate, a white precipitate separated, on cooling, which was found to contain calcium. Calcium tartrate was suspected. It was dissolved in acetic acid and treated with ammoniacal silver nitrate solution from which it deposited silver in the form of a mirror upon boiling. The free acid was precipitated by calcium hydroxide in the cold (distinction from citric acid).

The residue left after treating with boiling alcohol was tested with ammoniacal silver nitrate solution but it did not precipitate silver and was not precipitated by calcium hydroxide in the cold, though it was precipitated on heating.

The free acid was crystallized later and the rhombic prisms of citric acid identified.

SUMMARY.

Adlumia cirrhosa contains at least five distinct alkaloids as follows:

(1) Protopine, $C_{20}H_{19}NO_5$, melting-point 204°-205° C.

(2) β-Homochelidonine, $C_{21}H_{23}NO_5$, melting-point 159° C.

(3) Adlumine, $C_{39}H_{39}NO_{12}$ or $C_{39}H_{41}NO_{12}$, melting-point 187°-188° C.

(4) Adlumidine, $C_{30}H_{29}NO_9$, melting-point 234° C.

(5) Unnamed, melting-point 176°-177° C.

Also tartaric and citric acids.

The investigation is being continued.

SCHOOL OF PHARMACY, UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 78].

3-NITROPHTHALYL CHLORIDE AND ITS ACTION WITH AMMONIA AND WITH AROMATIC AMINES.

BY VICTOR JOHN CHAMBERS.

Received April 6, 1903.

THE action of phosphorus pentachloride upon 3-nitrophthalic acid has been tried before, but the product isolated from the reaction mass has not been the acid chloride. Boroschek[1] obtained the anhydride of 3-nitrophthalic acid and also the anhydride of 3-chlorphthalic acid. Levi[2] obtained only the anhydride of 3-nitrophthalic acid.

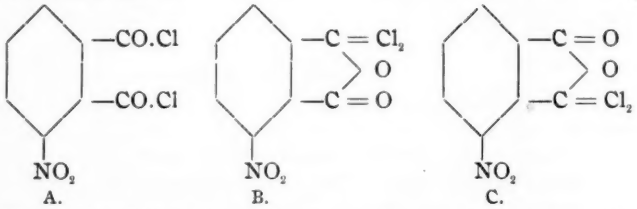
By using the process described in the experimental part, the author was able to obtain the acid chloride in the form of colorless, transparent, well-defined crystals melting at 76°-77° corr.

Phthalyl chloride, as is well known, has been assigned both a

[1] Inaug. Dissertation, 1901.

[2] Inaug. Dissertation, 1891.

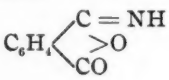
symmetrical and an unsymmetrical structure. The presence of the nitro group in 3-nitrophthalyl chloride introduces another possibility. If the chloride be symmetrical it can have only the one structure, A, but if a asymmetrical it can have either of the two forms B and C.



A. B. C.

The study of its action with various reagents, such as ammonia, substituted ammonias, alcohols and phenols, was undertaken in the hope of throwing some light upon this question. The action with ammonia and various substituted ammonias is reported in the present paper. The study of the action of alcohols and phenols is being carried on at the present time.

The action of ammonia upon phthalyl chloride has been tried under various conditions. Kuhara[1] passed dry ammonia gas over dry phthalyl chloride and obtained phthalimide as the result of a violent reaction. He also treated the chloride with aqueous ammonia and then the resulting solution with hydrochloric acid. On washing and crystallizing the product from alcohol, beautiful crystals were obtained that gave the same analytical results as phthalimide and yet showed different properties. He proposed the unsymmetrical structure



for the substance.

Auger[2] obtained a product he called the unsymmetrical amide of phthalic acid by treating the chloride with an excess of concentrated ammonia and evaporating over sulphuric acid. This amide, when treated with hydrochloric acid, gave a body isomeric with phthalimide.

Hoogewerff and Van Dorp[3] treated phthalyl chloride with a

[1] *Am. Chem. J.*, **3**, 26.
[2] *Ann. chim. phys.*, (6), **22**, 289.
[3] *Rec. trav. chim. Pays-Bas*, **11**, 84.

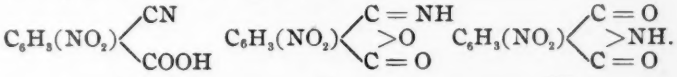
cold aqueous solution of ammonia, care being taken to prevent rise of temperature. After an excss had been added, the solution was acidified with hydrochloric acid. A crystalline substance separated that had the following properties: It melted at 180°-190°, solidifying again as the temperature rose and remelting at that of the imide; it had acid properties, forming a number of salts; it was easily decomposed by boiling with water and was changed to phthalamic acid by the action of concentrated sulphuric acid; it formed esters, and the ethyl ester was identical with that prepared by Miller from the *o*-cyanbenzoic acid made from anthranilic acid by the Sandmeyer reaction. The preparation of this acid from phthalyl chloride indicates the unsymmetrical structure for that chloride.

The action of dry ammonia upon dry 3-nitrophthalyl chloride was analogous to that upon the unsubstituted chloride. The imide was obtained.

The action of aqueous ammonia was different, however. No cyan acid could be obtained, the original 3-nitrophthalic acid being the only product. The reason for this was clear when it was found that the cyan acid, which was obtained by another method, was unstable in the presence of the slightest amount of water, passing to an acid ammonium salt of 3-nitrophthalic acid. This in turn gave the original nitrophthalic acid when acidulated. The action of aqueous ammonia upon a chloroform solution of the chloride, with cooling, was found to give a 3-nitrophthalamic acid.

The action of dry gaseous ammonia upon a dry ethereal solution of the chloride at a low temperature and subsequent treatment with hydrochloric acid gas gave a substance that had the same composition as 3-nitrophthalimide. This new substance melted at 99°-100° and then rearranged to the imide as the temperature was raised to 105°.

There are three possible structures that may be assigned to this body, leaving out of question for the moment the relation of the nitro group to the other groups. They are

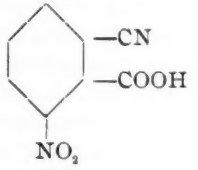


I. II. III.

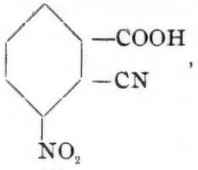
III is usually assigned to the well-known imide. Moreover, if ammonia gave, under the conditions described, a product to be

represented by either II or III it would be reasonable to expect that primary amines would give analogous bodies under like conditions. No such bodies could be obtained. It seems probable, therefore, that the substance in question is a nitrocyanbenzoic acid. One reason that Hoogewerff and Van Dorp gave for the cyan structure of the body they obtained by the action of ammonia upon phthalyl chloride was that the same body was formed by the introduction of CN in place of NH_2 in anthranilic acid. This proof could not be applied in this case as the compound is unstable in the presence of water. In that respect it differs from *o*-cyanbenzoic acid. For the same reason it could not be changed to the corresponding amic acid by treatment with concentrated sulphuric acid and then with water.

There are, however, two possible formulas that may be assigned to a cyan acid derived from 3-nitrophthalyl chloride:

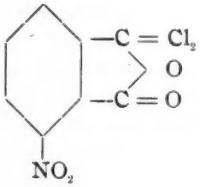


I.

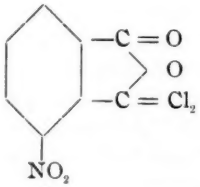


II.

These would be derived from the two theoretically possible chlorides:



A.

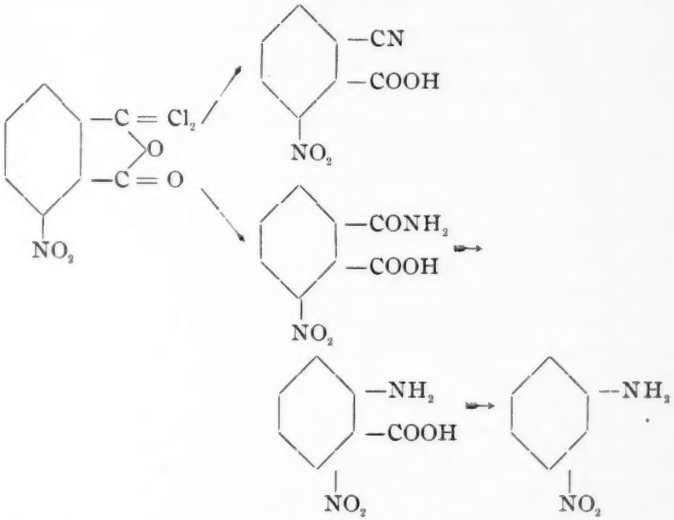


B.

It was found that the cyan acid obtained is to be given formula I and that, in consequence, formula A is the correct one for 3-nitrophthalyl chloride, if that body is to be assigned an asymmetrical structure.

While 3-nitrophthalyl chloride gave a nitrocyanbenzoic acid under certain conditions, it gave a nitrophthalamic acid under others. It is fair to assume that the CN group in one case and the $CONH_2$ group in the other are in the same position in the

molecule. The structure of this amic acid was obtained by the same method used by Kahn[1] to prove the structure of an acid methyl ester of 3-nitrophthalic acid. The nitrophthalamic acid was changed to a nitroanthranilic acid and its melting-point was that of the 2-nitro-6-aminobenzoic acid obtained by Kahn. Carbon dioxide was then eliminated from this acid and *m*-nitraniline obtained.



Van der Meulen[2] obtained phthalanilide by the action of aniline upon the hydrochloride of isophthalanil.

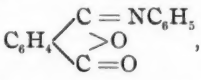
Rogow[3] shortly afterwards obtained it by the action of aniline upon phthalyl chloride.

Kuhara and Fukui[4] tried the action of a cold ethereal solution of aniline upon a similar solution of phthalyl chloride. A white solid was obtained which was washed with hydrochloric acid, ammonia, and water, and then extracted several times with small portions of boiling alcohol. It was crystallized from glacial acetic acid, and then from a large amount of boiling alcohol. A quantity of fine white needles was obtained. Analysis for nitrogen

[1] *Ber. d. chem. Ges.*, **35**, 631.
[2] *Rec. trav. chim. Pays-Bas*, **15**, 323.
[3] *Ber. d. chem. Ges.*, **30**, 1442.
[4] *Am. Chem. J.*, **26**, 454.

indicated a composition similar to that of the phthalanil. It differed markedly, however, from the known phthalanil.

Kuhara and Fukui gave it the structure



asymmetrical phthalanil. A similar compound was obtained from phthalyl chloride and orthotoluidine.

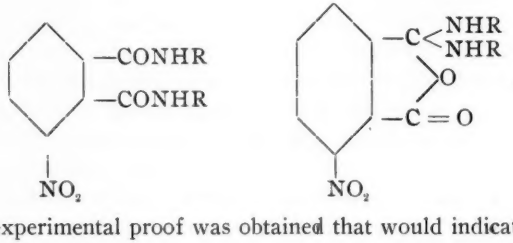
If a compound of this nature could be obtained when aniline is used instead of ammonia, it would point strongly to a similar structure for the so-called cyan acid.

The experiments of Kuhara and Fukui were tried with 3-nitrophthalyl chloride. A similar-looking product was obtained but analysis showed it to correspond to a 3-nitrophthalanilide. The experiment was tried a number of times with the same results. Paratoluidine, metanitroaniline and paranitraniline were substituted for aniline and similar products were obtained.

When the work was at this stage an article appeared by Hoogewerff and Van Dorp.[1] Their work indicated that Kuhara and Fukui really had phthalanilide which was transformed to phthalanil by the crystallization from glacial acetic acid.

That corresponded with the results obtained with 3-nitrophthalyl chloride and it only remained to show that the anilides obtained were also transformed to the anils by action of hot glacial acetic acid. This was found to be true in every case.

The action of a primary aromatic amine upon 3-nitrophthalyl chloride is then to introduce two molecules of the amine. The resulting compounds may have either of the two following structures:



No experimental proof was obtained that would indicate which of the two is the correct one.

[1] *Rec. trav. chim. Pays-Bas*, **21**, 339.

Experimental Part.

The chloride was made by the action of phosphorus pentachloride upon 3-nitrophthalic acid.

This acid was prepared by the Miller method as modified by Bogert and Boroschek.[1] 150 grams of phthalic anhydride were treated with a mixture of 225 grams of concentrated sulphuric acid and 225 grams of fuming nitric acid. The whole was heated in a roomy casserole on a water-bath until the nitrophthalic acids began to separate from the solution. About 20 cc. of water were then added and the whole heated a couple of hours longer. The mixture was then allowed to stand over night. The crystals were separated as completely as possible from the acid mother-liquor and dissolved in about 750 cc. of water. This solution was evaporated on a water-bath until a crust commenced to be formed. After standing quietly for from three to four hours, most of the 3-nitrophthalic acid separated as a hard crust on the walls of the container. A further small crop was obtained by evaporating the liquid again to two-thirds its bulk. The acid was purified by one recrystallization. Yield, about 50 grams.

Fifty grams of the acid in the state of a fine powder were mixed with 125 grams of phosphorus pentachloride and slowly heated in a casserole in a sulphuric acid bath. Action began at about 110°, the mass boiling violently. The heat was slowly raised to 140° or until the liquid began to develop a red color. On cooling, the reaction product became solid. This was reduced to a fine state of division and extracted with 400 cc. of carbon tetrachloride. After standing over night, most of the nitrophthalyl chloride separated as a mass of crystals somewhat red in color. To purify them they were powdered and crystallized twice from ligroin, boiling-point 60° to 80°. A fine white meal of crystals was obtained. Melting-point, 76°-77° (corr.).

The chloride separated as good-sized compact prisms when an ethereal solution was allowed to evaporate over sulphuric acid.

3-nitrophthalyl chloride is readily soluble in cold ether and chloroform and in warm carbon tetrachloride and ligroin. It is but little soluble in cold carbon tetrachloride or cold ligroin. It is quite stable when in the form of fair-sized compact crystals but is very unstable when in a fine state of division. The solvents used

[1] This Journal, **23**, 740.

in its purification must be perfectly dry or there is a considerable loss due to the formation of the anhydride.

Analyses gave the following results:

	Theory for $C_6H_3(NO_2)(COCl)_2$.	Found. I.	Found. II.
Carbon	38.74	39.00	....
Hydrogen	1.21	1.46	....
Nitrogen	5.66	5.91	....
Chlorine	28.55	28.53	28.26

ACTION OF AMMONIA.

Dry Chloride and Dry Ammonia.—A small quantity of the dry chloride was placed in a small flask and a current of dry ammonia passed over it. The reaction was violent, copious clouds of ammonium chloride being given off. The reaction mass became pasty and of a yellow color and very warm. The yellowish mass dissolved readily in a warm mixture of alcohol and acetone, giving small yellow crystals on standing. Melting-point, 213°-215°. Melting-point of 3-nitrophthalimide, 215°-216°.

Chloroform Solution of the Chloride and Dilute Ammonia Water.—A small quantity of the chloride was dissolved in about 75 cc. of chloroform. This was placed in a separatory funnel. Water and small pieces of ice were added and then successive small portions of dilute ammonia water until the odor of ammonia persisted after shaking and standing for ten minutes. The aqueous solution was separated from the chloroform and acidified with hydrochloric acid. Clusters of small, transparent plates separated on standing.

The melting-point of this substance was not constant. It melted to a clear liquid between 150° and 157°, according to rate of heating. A gas was given off at the same time that may have been confined air or a small amount of water coming from the decomposition of the substance. The substance solidified again at about 160° and remelted with vigorous evolution of water between 200° and 205°. When bubbling ceased, the product solidified again, if the temperature had not risen above 210° and remelted finally at 214°-215°, practically the melting-point of the imide. This behavior corresponds in part with that of 3-nitro-1-phthalamic acid.

To prove that it was such, it was transformed into 6-amino-2-

nitrobenzoic acid. The Hofmann method as used by Kahn[1] was followed. 2.1 grams of the amic acid were dissolved in 10 cc. of normal potassium hydroxide solution. The solution was well cooled and to it was added 0.5 cc. of bromine dissolved in 20 cc. of the normal alkali. The whole was well shaken and then treated with 30 cc. more of the alkali. On heating the yellow solution for an hour on a water-bath, its color changed to red. It was then placed in an ice-bath and carefully treated with 20.5 cc. of 2-N-hydrochloric acid, added drop by drop. The yellow mass that separated was crystallized from water. Beautiful leaves or sheaves of needle-like crystals were obtained melting with decomposition at 178°-180°. This corresponds with that of the 6-amino-2-nitrobenzoic acid obtained by Kahn. As a further proof, this body was changed to metanitraniline. One gram was dissolved in 10 cc. of methyl alcohol, and 0.5 cc. of concentrated sulphuric acid was added and the whole heated in a flask connected with a return condenser for seven hours. The reaction product was poured into a small amount of water and neutralized with sodium carbonate. The yellow solid that separated was crystallized twice from hot water. Fine yellow needles were obtained that melted at 112°. The melting-point of metanitraniline is 111°.

Dry Ethereal Solution of the Chloride and Dry Ammonia.—Two to three grams of the chloride were dissolved in 150 cc. of dry ether and placed in a freezing-mixture with a temperature of —5° to —10°. Dry ammonia gas was then passed in, whereupon the solution became milky. After the action was over, a stream of dry hydrochloric acid gas was passed through the mixture until it was no longer absorbed. The whole was filtered with suction. The clear, ethereal solution was diluted with 50 cc. of carbon tetrachloride and allowed to evaporate at room temperature in a current of dry air. Clusters of fine white needles were obtained. Nothing was found in the ethereal solution when the treatment with hydrochloric acid was omitted.

A small portion of this substance was placed in a melting-point tube and heated slowly. It melted to a clear liquid at 99°-100° and solidified again without apparent loss before the temperature reached 105°. It melted again without evolution of gas at 214°-215°.

[1] *Ber. d. chem. Ges.*, **38**, 631.

To show that the cyan acid rearranged to the imide without loss, a weighed portion of it was placed in a platinum crucible and heated in an air-bath for thirty minutes to a temperature of 125°. The rearrangement described above took place but the change in weight was less than a milligram. The fused mass was dissolved in a warm mixture of alcohol and acetone and gave crystals of the imide.

A small amount of the cyan acid was dissolved in dry ether, and ammonia gas passed through the solution. A white, amorphous mass was obtained and the ethereal solution left no residue. This body was thought to be the ammonium salt. It lost ammonia and passed to the imide when heated above 200°. No other salts could be formed, as the cyan acid is so unstable in the presence of water.

Hoogewerff and Van Dorp obtained phthalamic acid by the action of concentrated sulphuric acid upon *o*-cyanbenzoic acid. The same experiment was tried with the nitrocyanbenzoic acid but the results were not the same. 3-nitrophthalic acid was the only result.

Action of Water on the Cyan Acid.—Two grams of the acid were dissolved in 25 cc. of warm water. On cooling, thin plates separated. They melted at 140° to 145° with no evolution of water, solidified again and then remelted with evolution of water at 204°-205. The crystals were redissolved in a little water and kept warm, 60°-65°, for an hour. The crystals then obtained showed no sign of rearrangement but melted with evolution of water at 208°-212°. After all water had been driven off, the tube was allowed to cool. The contents were found to be the imide. The acid ammonium salt of 3-nitrophthalic acid was made and compared with the above. They were found to be identical.

Analysis of the nitrocyanbenzoic acid:

	Theory for $C_6H_3(NO_2)CN.COOH$.	Found.
Carbon	50.00	50.16
Hydrogen	2.08	2.10

ACTION OF PRIMARY AROMATIC AMINES UPON 3-NITROPHTHALYL CHLORIDE.

Action of Aniline.—A few grams of the nitrophthalyl chloride were dissolved in dry ether and cooled to —8°. A cold solution of aniline was added very slowly, care being taken to keep the temperature from rising above —5°. A pale yellow solid sepa-

rated at once. This was filtered off and washed with dilute hydrochloric acid and then with warm water. The white caseous residue was crystallized repeatedly from large amounts of boiling alcohol. The product separated in the form of white, fine needles that felted when filtered. Melting-point, 211°-212°, with decomposition. Analysis, as given below, showed the compound to be 3-nitrophthalanilide. It was insoluble in water, nearly so in cold alcohol, easily soluble in hot alcohol or glacial acetic acid. Prolonged boiling with water had no effect. Dilute sodium carbonate or hydroxide solution had no effect in the cold but liberated aniline when heated.

A small portion was heated for an hour to gentle boiling with glacial acetic acid. On cooling and diluting, crystals separated melting at 135°. Melting-point of 3-nitrophthalanil, 134°.

	Theory for $C_6H_3(NO_2)C_2O_2(NHC_6H_5)_2$.	Found.
Carbon	66.48	66.45
Hydrogen	4.16	4.34
Nitrogen	11.63	11.82

Action of Paratoluidine.—The results obtained by using paratoluidine instead of aniline were perfectly analogous to those described above. The reaction was carried on in a similar manner, the result being a mass of fine, white needles that could not be told from those obtained from aniline. Melting-point, 223°-225°, with decomposition. Analysis showed the compound to be 3-nitrophthal-*p*-toluide.

When heated with glacial acetic acid for a short time it was changed to 3-nitrophthal-*p*-tolil, melting-point, 152°-153°.

Analysis of 3-nitrophthal-*p*-toluide.

	Theory for $C_6H_3(NO_2)C_2O_2(NHC_6H_4CH_3)_2$.	Found.
Nitrogen	10.8	11.0

Action of Metanitraniline.—The experiment was carried on in the same way as with aniline. The reaction was not as rapid. The reaction-product was finally crystallized from a large amount of alcohol, giving a mass of small, white needles. They melted very poorly at 225° to 230°, with decomposition. Heating for two hours with glacial acetic acid dissolved them but also changed the substance to 3-nitrophthal-*m*-nitranil. Melting-point, 218°-219°.

Analysis of 3-nitrophthal-*m*-nitranilide.

	Theory for $C_6H_3(NO_2)C_2O_2(NHC_6H_4NO_2)_2$.	Found.
Carbon	53.21	53.19
Hydrogen	2.88	2.78

Action of Paranitraniline.—The experiment was carried out in the usual manner. No solid separated from the cold ethereal solution but did when it was allowed to warm to the room temperature. This was purified by the usual process of washing and crystallizing from warm alcohol. Small, warty masses separated. Further crystallization from alcohol gave small, pale yellow needles melting with decomposition at 197°-200°. It was probably a product analogous to those described above. No analysis was made.

Treatment with glacial acetic acid gave fine, yellow needles melting at 248° to 249° with slight decomposition.

The melting-point of 3-nitrophthal-*p*-nitranil obtained by Bogert and Boroschek was 249°.

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THE ACTION OF THE SODIUM SALTS OF DIBASIC ACIDS ON ANILINE HYDROCHLORIDE, AND OF ANILINE ON PHTHALYL CHLORIDE AND SUCCINYL CHLORIDE.

BY FREDERICK L. DUNLAP AND FREDERICK W. CUMMER.

Received March 24, 1903.

IN this Journal,[1] the results of the action of the sodium salts of monobasic acids on the hydrochloride of aniline and of other amines, were reported by one of us. This study has been further extended so as to include the sodium salts of dibasic acids, sodium phthalate and sodium succinate being selected for this experimental work.

When dry sodium phthalate and aniline hydrochloride are heated together, phthalanil is formed, while sodium succinate and aniline hydrochloride produce succinanilide and succinanil. Phthalanil and succinanil are not formed directly from the sodium phthalate or the sodium succinate and the aniline hydrochloride, but they are only the final products, phthalanilide and succinanilide being first formed, then undergoing, at the high temper-

[1] This Journal, **24**, 758 (1902).

ature at which the reaction is carried out, decomposition into aniline and the corresponding "anil."

1. $\begin{matrix}CH_2—COONa\\|\\CH_2—COONa\end{matrix} + 2C_6H_5NH_2.HCl =$

$$\begin{matrix}CH_2—CONHC_6H_5\\|\\CH_2—CONHC_6H_5\end{matrix} + 2NaCl + 2H_2O.^1$$

2. $\begin{matrix}CH_2—CONHC_6H_5\\|\\CH_2—CONHC_6H_5\end{matrix} = \begin{matrix}CH_2—CO\\|\\CH_2—CO\end{matrix}>NC_6H_5 + C_6H_5NH_2.$

3. $C_6H_4\begin{matrix}COONa\\COONa\end{matrix} + 2C_6H_5NH_2.HCl =$

$$C_6H_4\begin{matrix}CONHC_6H_5\\CONHC_6H_5\end{matrix} + 2NaCl + 2H_2O.^2$$

4. $C_6H_4\begin{matrix}CONHC_6H_5\\CONHC_6H_5\end{matrix} = C_6H_4\begin{matrix}CO\\CO\end{matrix}>NC_6H_5 + C_6H_5NH_2.$

In the products of the reaction between the sodium succinate and the aniline hydrochloride, both succinanilide and succinanil were isolated. The higher the temperature, the less the yield of succinanilide obtained. Phthalanilide, at its melting-point, passes readily into phthalanil, with the evolution of aniline vapors. In the case of the sodium phthalate and the aniline hydrochloride, no phthalanilide was isolated, phthalanil alone being obtained. Judging from analogy with the results obtained with the sodium succinate, phthalanilide must be first formed, then undergoing complete decomposition into phthalanil and aniline at a much lower temperature than that necessary for the complete conversion of succinanilide into succinanil and aniline; for at a temperature as low as 130°, the decomposition of phthalanilide is complete, provided this temperature is maintained for a sufficiently long time.

It should be noted that Verley[2] obtained succinimide by distilling a mixture of ammonium chloride and potassium succinate, the succinimide doubtless being produced by the potassium succinate

[1] It is quite likely that the sodium succinate and the sodium phthalate first form phenylammonium salts, as $\begin{matrix}CH_2—COONH_3C_6H_5\\|\\CH_2—COONH_3C_6H_5\end{matrix}$ and $C_6H_4\begin{matrix}COONH_3C_6H_5\\COONH_3C_6H_5\end{matrix}$, which, through loss of water, give respectively the phenylamides or anilides, as shown in equations 1 and 3.

[2] *Bull. Soc. Chim.*, [3], **9**, 692 (1893).

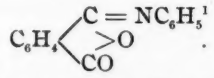
first forming ammonium succinate, then succinamide, and finally succinimide. At about 200°, succinamide decomposes into succinimide and ammonia.

So far as we have been able to ascertain, phthalanilide was first prepared by van der Meulen,[1] who obtained it by boiling an aqueous solution of the hydrochloride of the iso-methyl ester of phenylphthalamic acid. He found that phthalanilide melted at 251°-252° with decomposition. The year following the appearance of van der Meulen's work, Rogow[2] made a further study of phthalanilide. Rogow states in his paper that phthalanilide had not previously been prepared; but he evidently overlooked the results obtained by van der Meulen. Rogow prepared phthalanilide by the interaction of phthalyl chloride and aniline. He used, as he says, not only a sufficient quantity of aniline to form this compound, but also enough more to combine with the free hydrochloric acid evolved. Rogow used 15 grams of aniline and 5 grams of phthalyl chloride, in which the aniline is in large excess. In this reaction, Rogow used alcohol as a diluent for the aniline, and to this solution, well cooled by salt and ice, the phthalyl chloride was added. The product of this reaction, phthalanilide, he found to have a melting-point of 231°, at which temperature it underwent decomposition. This decomposition, as has been mentioned, is due to the splitting up of this compound into aniline and phthalanil.

In 1901, Kuhara and Fukui[3] reported the results of their study of the action of aromatic amines on phthalyl chloride, at different temperatures. Among the various experiments which they carried out, was one on the action of aniline at ordinary temperatures. This reaction was brought about by allowing phthalyl chloride and aniline, both diluted with ether, to react on one another in the molecular ratio of 1:3 respectively. The only product they mention having obtained, is phthalanil. When, however, this same reaction was carried out at —10°, the product obtained melted at 218°. and, upon analysis, gave results agreeing quite well for phthalanil. Phthalanil melts at 203°; and as the product obtained at the low temperature was capable of being converted into the compound with a melting-point of 203° by heating in a sealed

[1] *Rec. trav. chim. Pays-Bas*, **15**, 345 (1896).
[2] *Ber. d. chem. Ges.*, **30**, 1442 (1897).
[3] *Am. Chem. J.*, **26**, 454 (1901).

tube to 140° with *o*-xylol, they called their new product α-phenylphthalimide, and assigned it the following structure:



Kuhara and Fukui do not mention Rogow's work, whose results are at direct variance with theirs. Moreover, their methods are practically identical, except that Kuhara and Fukui used ether as a diluent while Rogow dissolved the aniline in alcohol. Kuhara and Fukui also fail to mention the work of van der Meulen,[2] who describes, under the name of phthalphenylisoimide, a compound having the same structure as their α-phenylphthalimide, but whose melting-point is 115°-117°.

This question of the products formed from the interaction of phthalyl chloride and aniline, we have resubmitted to experiment. The conditions under which we worked were identical with those of Kuhara and Fukui; namely, with ether as a diluent, at ordinary temperatures and at —10°, as well as with the same reacting masses.

Three products are formed when the reaction is carried on at ordinary temperatures: aniline hydrochloride, phthalanilide, and phthalanil. So far as the phthalanilide is concerned, our results are the same as Rogow's; relative to the phthalanil, our results coincide with those of Kuhara and Fukui. Rogow, however, mentions no product other than phthalanilide, while Kuhara and Fukui mention phthalanil alone. From this we judge that, even if other products were formed, the ones mentioned were the principal products formed.

When ether solutions of phthalyl chloride and aniline react at ordinary temperatures, a heavy white precipitate is formed, consisting of aniline hydrochloride and phthalanilide, while the ether filtrate from this precipitate contains practically no other product except phthalanil, and this in but very small amounts. From

[1] The experimental portion of this paper referring to the action of phthalyl chloride on aniline was done previous to the appearance of the work of Hoogewerff and Van Dorp (*Rec. trav. chim. Pays-Bas*, **21**, 339 (1902)), excepting the repetition of Kuhara and Fukui's work at low temperatures. The latter was finished previous to the appearance of the review of Hoogewerff and Van Dorp's work in the *Centralblatt*, 1903, I, 156, from which a knowledge of their work was first obtained. We have retained this portion of our experimental work as substantiating the findings of Hoogewerf and Van Dorp relative to the non-formation of α-phenylphthalimide from aniline and phthalyl chloride.

[2] *Rec. trav. chim. Pays-Bas*, **15**, 286 (1896).

these results, it appears that phthalanilide is the main product of the reaction. This experiment has been repeated a number of times, carrying out Kuhara and Fukui's directions as carefully as possible, but always with the results given above.

In carrying out this reaction at low temperatures, Kuhara and Fukui's directions were rigorously adhered to; but we have been unable to substantiate their results so far as the formation of the α-phenylphthalimide is concerned. Kuhara and Fukui treated the reaction product, after filtering off the ether, with water, hydrochloric acid, and ammonia. The residual product they extracted with boiling alcohol a number of times, to remove the phthalanil, after which the remaining product, α-phenylphthalimide, was purified by recrystallization from glacial acetic acid or alcohol, preferably the latter.

The results we obtained show that whatever phthalanil is formed in this reaction, remains in the ether filtrate, and that it is to be found there in only small amounts, mixed with phthalanilide. After treating the main product of this reaction with water, hydrochloric acid, and ammonia, we extracted the residue with boiling alcohol. In all, nineteen extractions had to be made with boiling alcohol before all this residue dissolved. From each one of these alcoholic fractions nothing but phthalanilide separated on cooling, with no trace of any other compound corresponding to α-phenylphthalimide, with a melting-point of 218°.

From the results we have given, it appears that the principal product formed from the interaction of phthalyl chloride and aniline is phthalanilide, while phthalanil occurs in but small amounts, the results being independent of the temperature. Aniline hydrochloride is likewise formed in considerable amounts under both conditions of temperature.

Phthalyl chloride, in a number of its reactions, deports itself as if it had an unsymmetrical structure. For example, with the Friedel and Crafts reaction, it yields diphenylphthalide;[1] on reduction with zinc and hydrochloric acid, phthalide is formed.[2] On the other hand, by reducing with glacial acetic and sodium amalgam, phthalyl chloride yields phthalyl alcohol,[3] a reaction very readily explained by the assumption of a symmetrical struc-

[1] *Ann. chim. phys.*, [6], **1**, 523 (1884).
[2] *Ber. d. chem. Ges.*, **11**, 237 (1878).
[3] *Ber. d. chem. Ges.*, **12**, 646 (1879).

ture for phthalyl chloride. The formation of phthalanilide and phthalanil from phthalyl chloride and aniline, is readily explained by accepting in this case the symmetrical structure for phthalyl chloride.

$$C_6H_4\begin{matrix}COCl\\COCl\end{matrix} + \begin{matrix}NH_2C_6H_5\\NH_2C_6H_5\end{matrix} = C_6H_4\begin{matrix}CONHC_6H_5\\CONHC_6H_5\end{matrix} + 2HCl$$

$$C_6H_4\begin{matrix}COCl\\COCl\end{matrix} + \begin{matrix}H\\H\end{matrix}\!\!>\!NC_6H_5 = C_6H_4\begin{matrix}CO\\CO\end{matrix}\!\!>\!NC_6H_5 + 2HCl.$$

Or, giving the complete equations, we have for the phthalanilide

$$C_6H_4(COCl)_2 + 4C_6H_5NH_2 = C_6H_4(CONHC_6H_5)_2 + 2C_6H_5NH_2.HCl;$$

while for the phthalanil we have the following:

$$C_6H_4(COCl)_2 + 3C_6H_5NH_2 = C_6H_4(CO)_2NC_6H_5 + 3C_6H_5NH_2.HCl.$$

From these completed equations we can see that, in the first case, we have the phthalyl chloride and the aniline in the molecular ratio of 1:4, while in the second it is only 1:3. We have found in our experiments that, where these compounds were brought together in the ratio of 1:3, the ether filtrate always contained some unchanged phthalyl chloride.

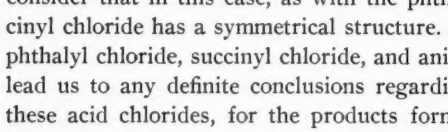
The reaction between succinyl chloride and aniline was also studied, but only at ordinary temperatures. In this case, the products formed were succinanilide and aniline hydrochloride, but no succinanil was isolated. If succinanil is formed in this reaction, it is only in quite small amounts.

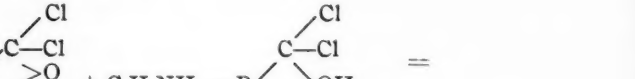
In the majority of its reactions, succinyl chloride acts as if it were γ-dichlorbutyrolactone. For example, it passes into butyrolactone on reduction;[1] it reacts with zinc ethyl to produce γ-diethylbutyrolactone;[2] with the Friedel and Crafts reaction it forms γ-diphenylbutyrolactone, but at the same time produces 10 per cent. of symmetrical dibenzoylethane.[3] The fact that symmetrical dibenzoylethane is formed, together with the γ-diphenylbutyrolactone, shows that succinyl chloride deports itself in this reaction like a mixture of the symmetrical and unsymmetrical forms, the latter being predominant. Inasmuch as succinanilide is the sole

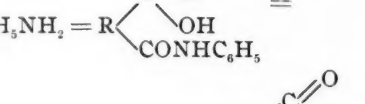
[1] *Ann. Chem.* (Liebig), **171**, 261 (1874); *J. prakt. Chem.*, [2], **25**, 63 (1882).
[2] *Ber. d. chem. Ges.*, **15**, 1851 (1882).
[3] *Ann. chim. phys.*, [6], **22**, 312 (1891).

product of the interaction of succinyl chloride and aniline, we can consider that in this case, as with the phthalyl chloride, the succinyl chloride has a symmetrical structure. These reactions with phthalyl chloride, succinyl chloride, and aniline, can not, however, lead us to any definite conclusions regarding the constitution of these acid chlorides, for the products formed may be explained from a standpoint of an unsymmetrical structure.

For example:







So far as we can see, there is no reason for believing that either phthalanilide or succinanilide have other than the symmetrical structure.

Experimental Part.

Action of sodium phthalate on aniline hydrochloride.

Dry sodium phthalate and aniline hydrochloride were ground up together in the proportion of one molecular weight of the former to two of the latter. The ground mixture, which developed the odor of aniline quite strongly, was heated in a sealed tube for six hours at 200°. There was no pressure on opening the tube. The solid contents of the tube were ground up several times with water, the water being decanted through a filter. The residue was treated in the same manner with dilute hydrochloric acid, and then given a final washing with water. The product thus obtained was

grayish in color. After several washings with small quantities of cold alcohol, the residue was recrystallized from boiling alcohol. The product thus obtained melted at 203°. The melting-point, crystalline form, and solubility in various solvents, were sufficient to identify this product as phthalanil. No phthalanilide was isolated from the products of this reaction; that is, at a temperature considerably below what must be the true melting-point of the phthalanil, this body breaks down into phthalanil and aniline, provided the heating be sufficiently prolonged.[1] From the product obtained by heating sodium phthalate and aniline hydrochloride to only 132° for five hours, no phthalanilide was isolated.

ACTION OF SODIUM SUCCINATE ON ANILINE HYDROCHLORIDE.

Sodium succinate and aniline hydrochloride in the molecular ratio of 1:2 respectively, were ground together and this mixture heated as in the case of the former experiment. The temperature during the heating reached 360°; and while the resulting mass was very dark-colored, both succinanilide and succinanil were obtained from it. A repetition of this experiment, where the heating of the sealed tube was carried on for four hours, and the maximum temperature reached was but 245°, gave a product much lighter in color than in the previous experiment, and yielded the same reaction products. There was a considerable amount of free aniline formed. The contents of this second tube, after washing with cold water and dilute hydrochloric acid, was extracted with boiling water. On cooling, this aqueous extract separated a large amount of slightly colored crystals. Recrystallization from hot water and treatment with bone-black gave a perfectly white product which crystallized in long needle-like crystals, having a melting-point of 150°.

The portion of the original product that was insoluble in water, was dissolved in boiling alcohol and treated with bone-black. This solution, on cooling, separated a crystalline product, which was further purified by several recrystallizations from alcohol. This product had a melting-point of 226°.

The compound with a melting-point of 150° gave 8.29 per cent. N. Calculated for $C_{10}H_9O_2N$, 8 per cent.

The product soluble in water was thus identified by its melting-

[1] For a discussion of the melting-point of phthalanilide, see the experimental portion of this paper on the action of phthalyl chloride on aniline.

point, and by analysis, as succinanil, while the substance obtained from the alcohol, which had a melting-point of 226°, proved to be succinanilide, and on analysis gave 10.7 per cent. N. Calculated for $C_{16}H_{16}O_2N_2$, 10.44 per cent.

In the experiment in which the mixture of sodium succinate and aniline hydrochloride were heated to 245°, 15 grams of the former substance and 24 grams of the latter were used. From the resulting product, 11.6 grams of succinanil and 3.3 grams of succinanilide were obtained. The higher the temperature at which this reaction is carried out, the larger the relative yield of succinanil.

ACTION OF PHTHALYL CHLORIDE ON ANILINE.

Freshly distilled phthalyl chloride and aniline (in the ratio of one molecular weight of the former to three of the latter) were each dissolved separately in about 300 cc. of ether which had been carefully dried over sodium wire. The aniline solution was slowly added, with constant stirring, to the ether solution of the phthalyl chloride, both solutions being at room temperatures. The reaction caused hardly any perceptible rise in temperature. The addition of the aniline solution produced a heavy white precipitate, which was filtered, washed with ether, and then dried. The ether filtrate, on standing over night, deposited crystals which were filtered off and purified by crystallization from alcohol. These crystals proved to be phthalanilide. The ether filtrate from these phthalanilide crystals, which had deposited on standing over night, was evaporated to dryness and the residue purified by crystallization from alcohol. This product had a melting-point of 203°, and analysis gave results showing that this product was phthalanil. The phthalanilide which separated from the ether solution, had no well-defined melting-point. According to the rapidity of heating, the melting-point could be varied from 20° to 25°, the product always melting with gas evolution (aniline). In its behavior in a melting-point tube, phthalanilide behaves very much like phthalic acid, of which substance no well-defined melting-point can be had, on account of the ease with which it breaks down into phthalic anhydride and water. If the temperature of 225° be held for some time, phthalanilide will finally melt with gas evolution; but, with the ordinary rapidity with which melting-points are taken, the melting-point of phthalanilide usually obtained by us lay some-

where between 240° and 250°, while occasionally the melting-point would run still higher. This variable melting-point is doubtless due to the production of more or less phthalanil (m. p. 203°) at a temperature below the true melting-point of the phthalanilide, which phthalanil, as soon as formed, lowers the melting-point of the whole mass.

The white precipitate obtained by the action of the aniline on the phthalyl chloride was, after drying, treated with hot water to remove the aniline hydrochloride. The residue was recrystallized from boiling alcohol, in which, however, it is not very soluble. The only product obtained was phthalanilide. Three analyses were made of this phthalanilide, the per cents. of nitrogen found being 9.11, 9.08, and 9.11, instead of 8.86 per cent. as calculated.

ACTION OF SUCCINYL CHLORIDE ON ANILINE.

In this experiment, freshly distilled succinyl chloride and aniline, both diluted with dry ether, were allowed to interact at ordinary temperatures. An excess of aniline a little greater than the molecular ratio of one of succinyl chloride to three of aniline, was found necessary in order to completely decompose the succinyl chloride. More heat seemed to be developed by this reaction than in the case where phthalyl chloride was used. In fact, if the ether solution of the aniline was added too fast to the ether solution of the succinyl chloride, sufficient heat was developed to cause the solution to boil. The heavy white precipitate produced, was filtered, washed with ether, and dried. Then after thoroughly washing with water, in order to free the product from aniline hydrochloride, the residue was purified by crystallization from alcohol. The pure product had a melting-point of 226.5°, and on analysis proved to be succinanilide. Found, 10.53 per cent. N. Calculated, 10.45 per cent.

The ether filtrate was evaporated to dryness, and an oily product, smelling strongly of aniline, was obtained, showing that an excess of aniline had been used in the reaction. This residue was, however, small in amount. On standing for some time *in vacuo* over sulphuric acid, this oily product became of a pasty consistency. No succinanil was obtained from this residue. If succinanil is formed by the interaction of succinyl chloride and aniline under the conditions we used, it is only in quite small amounts.

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN,
March 1, 1903.

SOME DERIVATIVES OF *p*-SULPHOCINNAMIC ACID.

By F. J. Moore.

Received April 15, 1903.

The action of fuming sulphuric acid upon cinnamic acid was first thoroughly studied by Rudnew,[1] who isolated from the sulphonation mixture, two acids: one, the now well-known *p*-sulphocinnamic acid, which is the principal product of the reaction; and the other, an isomer which he called a meta-compound. Since that time the true *m*-sulphocinnamic acid has been prepared synthetically by Kafka,[2] and as its properties do not agree with those of the acid described by Rudnew, it is probable that the latter is an ortho-compound.

Rudnew's method of isolating these acids from the sulphonation mixture was the familiar one of treating the products of the reaction with barium hydroxide. The sulphonic acids were then separated from each other, and from the masses of barium sulphate produced, by crystallization from water. This method is tedious at best, and when one only wishes to prepare the para acid (as in the present investigation) it is better to take advantage of the fact (apparently heretofore overlooked) that this acid crystallizes spontaneously from the sulphonation mixture upon appropriate dilution with water. The *p*-sulphocinnamic acid used in this investigation was prepared in accordance with the following procedure. 150 grams of fuming sulphuric acid (containing 15 per cent. to 20 per cent. anhydride) are placed in a flask and 50 grams of finely ground cinnamic acid are introduced in small portions with constant shaking. The temperature rises during the reaction, and the quantities of cinnamic acid added are so regulated that the flask in which the sulphonation takes place shall not become uncomfortably warm to the hand. At the close, the reaction becomes sluggish, and may be concluded by heating for fifteen or twenty minutes on the water-bath. At this point the mixture should not be dark brown in color and should smell only faintly of sulphur dioxide. When cold, it is diluted with about three times its volume of water, and allowed to stand over night. If crystals of the *p*-sulphocinnamic acid are at hand, they should be added as soon as the diluted acid has become cold. Crystalliza-

[1] Rudnew: *Ann. Chem.* (Liebig), **173**, 8.

[2] Kafka: *Ber. d. chem. Ges.*, **24**, 746.

tion then begins almost at once—usually at the bottom of the flask—but proceeds very slowly. It is seldom complete in less than ten hours, but at the end of that time the contents of the flask usually seem entirely solidified. It is usually best to determine the proper amount of dilution by experiment, with small portions, as different sulphonations, under apparently identical conditions, sometimes require slightly different treatment. The crystals thus obtained are filtered off and dried by suction. They are sufficiently pure for most purposes. A perfectly pure product is best obtained by dissolving the crude acid in water, precipitating the acid barium salt by means of a solution of barium chloride, purifying this by crystallization, and finally decomposing it with the calculated amount of sulphuric acid. On evaporation, the acid is obtained in the long four-sided prisms described by Rudnew. He describes these crystals as stable in the atmosphere,—an observation which I cannot confirm, possibly on account of the greater dryness of the American climate. The crystals which I obtained were very large and well formed, often showing beautiful twin-formation, but they weathered rapidly on exposure to the air. The acid was characterized by the preparation of the amide described by Palmer,[1] and by the crystalline form of the acid barium salt described by Rudnew, which crystallizes in beautiful long needles very difficultly soluble in cold water.

Previous investigators do not seem to have noticed the fact that this acid forms very insoluble acid salts with a number of the aromatic amines, and these salts offer a more convenient means of characterizing this acid than either of the methods mentioned above. Only the aniline salt was analyzed. This may be prepared by treating a solution of the acid, or any of its more soluble salts, with a solution of aniline hydrochloride. A crystalline precipitate appears at once, and on recrystallization from hot water, the salt shows a marked tendency to form large radially arranged aggregates. These crystals melt at 246° (uncorrected) and their composition is established by the following analysis.

Calculated for $C_{15}H_{15}O_5NS$: C, 56.08 per cent.; H, 4.67 per cent.; N, 4.35 per cent. Found: C, 56.07 per cent.; H, 4.82 per cent.; N, 4.77 per cent.

Acid Sodium Salt.—In the preparation of sulphocinnamic acid,

[1] **Palmer**: *Am. Chem. J.*, **4**, 163.

as above described, a somewhat larger yield may be obtained by pouring the mother-liquor from the crystals of free acid into a saturated solution of sodium chloride. The acid sodium salt then separates out, and may be purified by crystallization from water. As this salt has not been heretofore described, the following analytical data are appended:

Calculated for $C_9H_7O_5SNa,2H_2O$: Na, 8.04 per cent.; H_2O, 12.59 per cent. Found: Na, 7.93 per cent.; H_2O, 12.59 per cent. at 110°.

p-Sulphodibromhydrocinnamic Acid.—*p*-Sulphocinnamic acid absorbs two equivalents of bromine with great readiness, even in aqueous solution. For this purpose, the acid is dissolved in just enough cold water to make a clear solution, and the calculated amount of bromine is added in portions of about a cubic centimeter with constant shaking. Any excess of bromine is finally removed by a current of air. A large part of the bromine addition product now separates as a fine, white, crystalline powder, and an almost quantitative yield may be obtained by evaporation of the mother-liquor in the cold. The first portions of the acid to be precipitated are very pure, but, for purposes of analysis, the acid was recrystallized from water, and then air-dried.

Calculated for $C_9H_8Br_2S,2H_2O$: C, 25.15 per cent.; H, 2.83 per cent.; Br, 37.20 per cent.; S, 7.54 per cent.; H_2O, 8.25 per cent. Found: C, 25.21, 25.22, 25.38 per cent.; H, 2.85, 3.00, 2.79 per cent.; Br, 37.15, 37.65, 37.32 per cent.; S, 7.93, 7.77, 7.59 per cent.; H_2O, 6.05, 7.73, 6.68 per cent.

One hundred parts of saturated solution at 20° contain from 53 to 57 parts of solid acid.

It is evident from the above, that the acid does not give up quite all its water of crystallization at 110°, but continued heating at a higher temperature results in slight decomposition as shown by a brown discoloration of the material.

Barium Salt.—The most characteristic inorganic salt of this acid is the acid barium salt, which is precipitated when a solution of the acid is treated with barium chloride. It crystallizes in short colorless needles.

Calculated for $C_{18}H_{14}O_{10}S_2Br_4Ba,4H_2O$: C, 21.98 per cent.; H, 2.24 per cent.; S, 6.36 per cent.; Br, 32.55 per cent.; Ba, 13.94 per cent.; H_2O, 7.32 per cent.

Found: C, 21.64 per cent.; H, 2.40 per cent.; S, 6.64 per cent.; Br, 32.52 per cent.; Ba, 14.37 per cent.; H_2O, 8.10 and 7.34 per cent.

100 parts saturated solution contain 2.7 parts of solid salt.

Copper Salt.—When concentrated solutions of the acid are treated with a concentrated solution of copper sulphate, a white precipitate is obtained. This may be recrystallized from water, and then forms small wart-like aggregates of a pale greenish white color, which show some tendency to decompose when half dry, but which, when perfectly dry, are quite stable. The substance is evidently an acid salt.

Calculated for $C_{18}H_{14}O_{10}Br_4S_2Cu,2H_2O$: Br, 36.63 per cent.; S, 7.32 per cent.; Cu, 7.28 per cent.; H_2O, 4.12 per cent.

Found: Br, 35.38, 35.10 per cent.; S, 7.25, 7.39 per cent.; Cu, 7.11, 7.43 per cent.; H_2O, 4.50 per cent. at 110°.

The results for bromine can hardly be considered satisfactory, but the salt is not well characterized, and another analysis did not seem worth while. It is very soluble in water.

Sodium Salts.—The acid sodium salt was prepared by the action of bromine upon the acid sodium salt of *p*-sulphocinnamic acid. It is a white crystalline powder.

Calculated for $C_9H_7O_5BrSNa,3H_2O$: Br, 34.48 per cent.; S, 6.90 per cent.; Na, 4.95 per cent.; H_2O, 11.63 per cent.

Found: Br, 34.76 per cent.; S, 7.30 per cent.; Na, 5.21 per cent.; H_2O, 11.69 per cent.

The neutral sodium salt was prepared by treating a solution of the free acid with sodium hydroxide until the solution was neutral to phenolphthaleïn. This salt crystallizes in needles very soluble in water.

Calculated for $C_9H_6O_5Br_2SNa_2,4H_2O$: H_2O, 14.03 per cent. Found: H_2O, 14.02 per cent.

Ammonium Salt.—When a solution of the free acid is treated with an excess of ammonia and evaporated in a desiccator over sulphuric acid, crystals appear which probably consist of the neutral ammonium salt, but an analysis was impracticable, as the salt is not stable, and the products of decomposition have not yet been determined. They will be an object of subsequent study.

Amide.—*p*-Sulphocinnamic acid and its salts react vigorously

with phosphorus pentachloride. The acid chloride thus formed has not been isolated, but the reaction-mixture was poured into dilute ammonia with the object of preparing the amide. A product was thus formed which crystallizes from hot water (in which it is soluble only with difficulty) in bulky scales. These melt sharply at 208° (uncorrected) and decompose just above the melting-point with evolution of bromine. This substance is doubtless the diamide in which both hydroxyl groups of the acid are replaced by amido-groups, although the analytical results (especially for nitrogen) have never been entirely satisfactory. The yield is poor —never better than 10 per cent. of the material used. Other less well-characterized products sometimes appear, and the amide seems to undergo some decomposition in the treatment with hot water necessary for recrystallization.

Calculated for $C_9H_{10}O_3N_2BrS$: N, 7.25 per cent; Br, 41.45 per cent.; S, 8.29 per cent.

Found: N, 8.22 per cent.; Br, 41.18 per cent.; S, 8.44 per cent.

Salts with Organic Bases.—When the acid is treated with aniline hydrochloride in aqueous solution, a white crystalline precipitate is obtained. Salts of most of the aromatic amines seem to behave in a similar way. Among those tried were aniline, dimethyl aniline, diethyl aniline, quinoline, α- and β-naphthyl amine phenylene diamine, and diphenyl amine. It should be noted that neither pyridine nor any of the aliphatic amines yield similar precipitates, so far as tried. Most of the salts of the aromatic amines thus obtained crystallize well, and the aniline, dimethyl aniline, and diethyl aniline salts also melt sharply. They therefore furnish the most convenient method of characterizing the acid. The three salts just mentioned are all acid salts, as is shown by the analyses given below; the others probably have similar composition, but were not analyzed. All may be crystallized from hot water, the dimethyl aniline salt producing the best-formed crystals.

Aniline salt, white needles, melting-point 192°.

Calculated for $C_{15}H_{15}O_5NBr_2S$: Br, 33.27 per cent.; S, 6.65 per cent.; N, 2.91 per cent.

Found: Br, 33.52, 33.43 per cent.; S, 7.01, 6.82 per cent.; N, 3.05, 3.27 per cent.

One part of salt dissolves in 67 parts of water at room temperature.

Diethyl aniline salt, melting-point 160°.

Calculated for $C_{19}H_{23}O_5NBr_2S$: C, 42.45 per cent.; H, 4.28 per cent.; N, 2.61 per cent.; Br, 29.80 per cent.; S, 5.96 per cent.

Found: C, 42.25 per cent.; H, 4.19 per cent.; N, 2.80 per cent.; Br, 29.63, 29.89 per cent.; S, 6.14, 6.13 per cent.

Dimethyl aniline salt, clear prisms melting at 150°.

Calculated for $C_{17}H_{19}O_5NBr_2S$: C, 41.02 per cent.; H, 3.73 per cent.; N, 2.75 per cent.; Br, 31.44 per cent.; S, 6.29 per cent.

Found: C, 40.59 per cent.; H, 3.89 per cent.; N, 3.25 per cent.; Br, 31.09 per cent.; S, 6.31 per cent.

Action of Silver Nitrate upon p-Sulphodibromhydrocinnamic Acid.—When an aqueous solution of the free acid or its salts is treated with a solution of silver nitrate, a precipitate is formed. This is sometimes curdy, but when both solutions are concentrated, a separation of short needle-like crystals is sometimes observed. This may be a silver salt of the organic acid, but, if so, it is extremely unstable, and in a few minutes at longest, the precipitate consists entirely of silver bromide. In dilute solutions in the cold, it may be determined by a rough titration that precipitation ceases when one molecule of silver nitrate has been added to one of the acid. Salts of lead and mercurous mercury act in this respect like silver. The result, in any case, seems to be a splitting-off of one molecule of hydrobromic acid from the side-chain, resulting in the formation of a *p*-sulphobromcinnamic acid. This acid has not yet been isolated, and even the salts are difficult to obtain. When silver nitrate is used to remove the hydrobromic acid, the nitric acid set free by the reaction seems to have an oxidizing action upon the new product formed. The substitution of other salts for silver nitrate has hitherto involved somewhat similar difficulties. On one occasion, when the acid sodium salt of *p*-sulphodibromhydrocinnamic acid had been treated with dilute silver nitrate solution, the silver bromide produced filtered off, and the filtrate evaporated in a vacuum desiccator over sulphuric acid; crystals were obtained, for whose purity no guarantee could be given, but the analytical data presented below would seem to indicate the presence of an acid sodium salt of *p*-sulphomonobromcinnamic acid. Nothing conclusive is claimed for the results.

0.1996 gram substance yielded 0.1037 gram AgBr and 0.1352 gram $BaSO_4$.

0.2654 gram substance lost 0.0085 gram at 135°.

Calculated for $C_9H_6O_5BrSNa,H_2O$: Br, 23.05 per cent.; S, 9.22 per cent.; H_2O, 5.19 per cent.

Found: Br, 22.11 per cent.; S, 9.30 per cent.; H_2O, 3.54 per cent. at 135°.

Action of Aqueous Hydrobromic Acid upon p-Sulphocinnamic Acid.—The fact that sulphocinnamic acid adds bromine in aqueous solution, rendered it probable that hydrobromic acid might be added with equal readiness. Some of the acid was therefore dissolved in concentrated hydrobromic acid. It is only soluble with difficulty in this medium, and the acid was warmed to hasten solution. A few hours later, the flask was found to be traversed in all directions by thin, needle-like crystals, whose length seemed only limited by the dimensions of the flask. These crystals were filtered off, the mother-liquor removed as much as possible by suction, and the crystals air-dried. Washing with pure water was impracticable on account of their solubility in this medium. It was supposed at first that these crystals represented the hydrobromic acid addition product sought. A bromine determination, however, showed that the bromine content was small and variable, and evidently due only to contamination from the mother-liquor.

0.1567 gram substance yielded 0.0034 gram AgBr.

0.1763 gram substance yielded 0.0068 gram AgBr.

This is equivalent to 0.92 per cent. and 1.64 per cent. Br respectively.

The possibility remained that the crystals might be unchanged *p*-sulphocinnamic acid. This seemed at first very improbable as they are very different in appearance from the large four-sided prisms with oblique ends which this acid forms when crystallized from water. A further difference existed in the fact that while the latter weathered rapidly on exposure to the air, the new crystals were very stable in the atmosphere, and only lost water over sulphuric acid. This could be accounted for if the new crystals contained less water than the old. This proved to be the case. The analysis shows that the former contain 3 molecules of water of crystallization while the latter, as described by Rudnew, contains 5. The chemical identity of the two substances was shown by dissolving the new crystals in water and adding aniline hydro-

chloride. The acid aniline salt above described, melting at 246°, was precipitated.

Calculated for $C_9H_8O_5Br_2,3H_2O$, 19.22 per cent.

Found: H_2O, 20.36 and 20.00 per cent at 110°.

The results are slightly high, but when it is remembered that these crystals contain some hydrobromic acid, which would also be lost at this temperature, they may be considered conclusive.

The above results are published on account of a temporary interruption of the work. It will, however, be again taken up, and I desire to reserve the field of the halogen derivatives of *p*-sulphocinnamic acid for some time longer.

My hearty thanks are due to my assistant, Mr. L. A. Salinger, who did most of the manipulative work, and conducted most of the analyses recorded in this paper.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
April 13, 1903.

THE ANALYTICAL CONSTANTS AND COMPOSITION OF MYRTLE WAX.

BY WARREN RUFUS SMITH AND FRANK BERTRAM WADE.

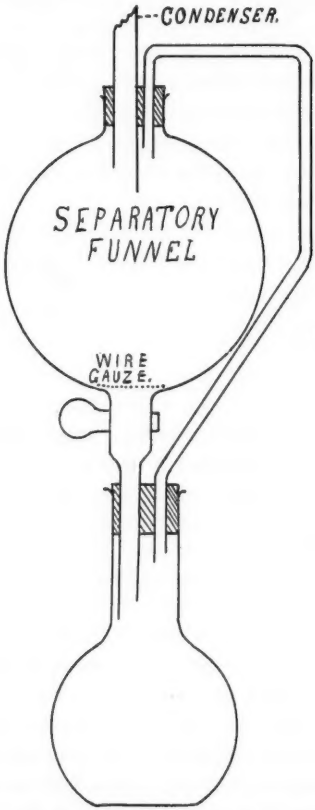
Received April 10, 1903.

MYRTLE wax, also known as laurel wax or bayberry tallow, is a fat of minor commercial importance obtained from the fruit of *myrica cerifera,* a shrub common along the North Atlantic seacoast and in other sections of this country. The statements regarding its composition are somewhat contradictory. The general books of reference state that it is mainly free palmitic acid with about 20 per cent. palmitin. Some state that it also contains lauric acid and others that it contains stearic and myristic acids. The first of these statements is due to Moore,[1] the second to Chevreul.[2]

On the other hand, the works on oil and fat analysis state that myrtle wax is a triglyceride with a small amount of free fatty acid, and give low "acid values" in support of these statements. Benedict[3] states that it is composed mainly of palmitin with some myristin and stearin. Lewkowitsch[4] says that in addition to the

[1] *Am. J. Sci. and Arts*, 2nd series, **33**, 313.
[2] *Compt. rend.*, **20**, 38.
[3] "Analyse der Fette," 3rd ed., p. 535.
[4] "Chemical Analysis of Oils, Fats, and Waxes," p. 542.

above it contains a small amount of oleic acid. Allen,[1] while he does not give the composition of myrtle wax, says that it contains 0.12 per cent of free acid (in terms of palmitic acid). Bayberry



wax has been suggested and used[2] as a convenient source of palmitic acid so that the question of its composition becomes a matter of importance.

The following experiments were undertaken for the purpose of obtaining additional evidence on this question. The material used was obtained by us directly from the berries by extraction with

[1] "Commercial Organic Analysis," 3rd ed., Vol. II, Part 1, p. 169.
[2] Chittenden and Smith: *Am. Chem. J.*, **6**, 218.

petroleum ether. The extractor used was devised from ordinary laboratory apparatus and worked so well that we append a sketch of it for the benefit of any one who has occasion to extract quantities of material larger than can be contained in a Soxhlet's extractor of ordinary size.

The following constants were obtained by the methods given in Lewkowitsch's "Chemical Analysis of Oils, Fats and Waxes."

Specific gravity, $\frac{22°}{15.5}$	0.9806
Specific gravity, $\frac{99°}{15.5}$	0.878
Melting-point	48° [1]
Solidifying point	45°
Saponification value	217
Iodine value (Hübl)	3.9
Reichert-Meissl number	0.5
Acid number	30.7
Refractive index, 80°	1.4363

These figures show the absence of oleic and volatile acids and agree with the assumption that myrtle wax is mainly palmitin with some lower glyceride and a small amount of free acid. By crystallizing four times from petroleum ether pure palmitin was obtained, melting-point, 62.5; saponification value, 209.4; refractive index, 1.4380 at 80°.

Like most fats, myrtle wax shows a change of melting-point and other constants on standing. The berries from which the above wax was obtained were picked in September and the wax was extracted and its constants obtained in November. On extracting another portion in March, a melting-point of 54° was obtained. Wax from berries obtained in August and extracted in March melted at 55.4°. A redetermination in March of the melting-point of the main portion gave 52.5°, a rise of 4.5° in four months. A specimen of wax about four years old melted at 57° and solidified at 58.3°. These rather high figures led us to suspect that stearin might be present but, after repeated crystallization from alcohol, practically pure palmitin was obtained, melting at 61.5° and giving a saponification value of 206.7. The absence of stearic acid was finally shown by the fact that Hehner and Mitchell's method gave no stearic acid even on salting with a crystal of stearic acid and

[1] "Method of Allen," Vol. II, Part I, p. 34.

allowing to stand for a further period of ten hours at 0°. We conclude therefore that myrtle wax contains no stearin and that the high melting-point of the older material is due to the obscure change which takes place in many fats on standing. We hope to study this change in myrtle wax further and determine how the constants, other than melting- and solidifying-points, are affected thereby.

LEWIS INSTITUTE, CHICAGO, ILL.,
March, 1903.

THE ANALYSIS OF BRONZES AND BEARING METALS.[1]

BY H. E. WALTERS AND O. I. AFFELDER.

Received April 11, 1903.

In the laboratory with which the writers are connected, many bronzes and bearing metals are analyzed, and it was thought that the methods which are used might prove of interest to the members of this Section.

While the scheme contains much that is old, we wish to call particular attention to the volumetric method for determining lead, as the results obtained by it are as reliable as those obtained by the sulphate method.

BRONZES.

The analysis of bronzes is carried out as follows:

Weigh 1 gram of the sample (0.5 gram, if the lead is over 15 per cent.) into a No. 2 beaker, cover with a watch-glass, add 10 cc. nitric acid (sp. gr. 1.42) and warm until all is dissolved. When in solution, add 40 cc. hot water and boil five minutes, filter, wash with 2 per cent. nitric acid, burn and weigh as SnO_2. To the filtrate add 25 cc. strong ammonia and heat to boiling, then add about 5 grams ammonium persulphate and boil from five to ten minutes. Make acid with sulphuric acid, filter and wash with hot water. The lead will remain on the filter as lead peroxide. Transfer the precipitate and filter to the beaker in which precipitation was made, add water and stir well to disintegrate the filter-paper. Dilute to 600-700 cc. with cold water, add about 3 grams potassium iodide and some starch solution. When all the iodide is dissolved, add 10 cc. hydrochloric acid (1:1), stir well and titrate

[1] Read before the Pittsburg Section of the American Chemical Society at the first monthly meeting, March 19, 1903.

with one-twentieth normal sodium thiosulphate until the solution changes from the dirty and dark yellow color to a bright lemon-yellow; or, an excess of sodium thiosulphate may be added and the excess titrated with one-twentieth normal iodine solution until the color changes from the bright yellow of the lead iodide present to the dirty and dark yellow. The number of cubic centimeters of sodium thiosulphate used multiplied by 0.5175 will give the percentage of lead. Where speed is not desirable, the lead may be determined by adding sulphuric acid to the filtrate from the oxide of tin, or the lead and copper may be deposited with the electric current.

Dilute the filtrate from the lead peroxide to 500 cc., heat to boiling and add 50 cc. of a 20 per cent. sodium thiosulphate solution,[1] boil five minutes, filter, wash with hot water, burn, and weigh as CuO.

Copper may also be determined by the following method, which is a modification of Low's method.[2] Dissolve 0.5 gram of the sample in 10 cc. nitric acid (sp. gr. 1.42). When in solution, dilute with cold water and add sodium carbonate until the solution is alkaline, make acid with acetic acid and add about 3 grams potassium iodide and some starch solution. Titrate with a sodium thiosulphate solution which has been standardized with pure copper.

Oxidize the filtrate from the copper sulphide thrown down by the thiosulphate as described above, with nitric acid and potassium chlorate and evaporate until the volume is about 300 cc. Make a basic acetate separation and determine iron or aluminum by the well-known methods. Make the filtrate from the iron or aluminum strongly alkaline with ammonia, heat to boiling and add ammonium persulphate, boil five minutes, filter, and wash with hot water, burn and weigh as Mn_3O_4.

To the filtrate from the manganese add ammonium phosphate in excess, heat to boiling and add hydrochloric acid until there is but a slight excess of ammonia, boil five minutes, filter and wash with hot water. The precipitate may be dried and weighed as $ZnNH_4PO_4$, or it may be filtered on a Gooch crucible and ignited to $Zn_2P_2O_7$. It may also be titrated with standard acid and alkali.[3]

[1] Nissenson and Neumann: *Chem. Ztg.*, 1895, p. 1591.
[2] *Eng. and Min. J.*, 1895.
[3] Walker: This Journal, **23**, 468.

Any nickel which may be present will be found in the filtrate from the zinc and may be precipitated as sulphide and ignited to NiO. If manganese is present in small quantities, it may be determined in a separate portion by the following method: Weigh 0.2 gram of the sample into a suitable test-tube, add 10 cc. nitric acid (sp. gr. 1.20) and warm until the sample is dissolved and all nitrous fumes are driven off. Add 15 cc. silver nitrate solution (1.33 grams of the salt to 1 liter of water) and about 0.5 gram ammonium persulphate, warm until the manganese is oxidized to permanganic acid, cool, transfer to a beaker, dilute to 100 cc., and titrate with standard sodium arsenite or hydrogen peroxide until disappearance of the pink color.

DETERMINATION OF PHOSPHORUS.

To determine phosphorus dissolve 1 gram of the sample in 5 cc. fuming nitric acid, evaporate to expel most of the free acid, add 10 cc. concentrated hydrochloric acid and evaporate to dryness. Dissolve the residue in hydrochloric acid and water, heat to boiling and precipitate lead, tin, and copper with metallic zinc, filter and wash with hot water. To the filtrate add some iron solution free from phosphorus and 10 cc. nitric acid (sp. gr. 1.42), boil a few minutes and then precipitate with ammonia and filter to separate most of the zinc, dissolve the precipitate in hot nitric acid (sp. gr. 1.20) and precipitate the phosphorus with molybdate solution. The yellow precipitate may be weighed or titrated.

BEARING METALS.

If the sample is high in tin and low in lead, proceed as outlined for bronzes, but if the sample is high in lead and contains antimony, proceed as suggested by Mr. George Hopkins, chemist to the Carrie Furnaces of the Homestead Steel Works, he having found that the addition of an excess of pure tin will insure the complete separation of the antimony with the oxide of tin. Weigh 0.5 gram of the sample and 0.25 gram of pure tin into a tall No. 2 beaker, cover with a watch-glass, add 20 cc. nitric acid (sp. gr. 1.33) and boil down to pastiness, add 40 cc. hot water and boil a few minutes, filter and wash with 2 per cent. nitric acid, burn and weigh as $SnO_2 + Sb_2O_4$. The filtrate is made strongly alkaline with caustic potash and the lead oxidized by adding about 10

grams ammonium persulphate. The rest of the analysis is carried out as outlined for bronzes.

To determine antimony[1] weigh 1 gram of the sample and 1 gram potassium iodide into a No. 2 beaker, add 80 cc. hydrochloric acid (sp. gr. 1.10) and boil gently for one hour, filter on a weighed paper or Gooch crucible and wash with dilute hydrochloric acid and then with hot water until free from chlorides. Wash once with alcohol, dry for one hour at 100° C. and weigh. The increase in weight is metallic antimony. Calculate this to Sb_2O_4 and subtract from the weight of the mixed oxides; calculate the tin from the weight of stannic oxide found and subtract the tin which was added.

Arsenic is determined in a separate portion by any of the well-known distillation methods.

Bismuth, if present, would be found with the copper sulphide, and can be determined by dissolving the sulphides in nitric acid, and precipitating the bismuth with ammonia.

REMARKS.

It will be noted that the filtrate from the tin in bronzes is made alkaline with ammonia, while in bearing metals, caustic potash is used. If caustic potash be used for bronzes, the copper would be precipitated and the lead would not be completely oxidized, while if the filtrate of a high lead-bearing metal is made alkaline with ammonia the lead hydroxide precipitate would be of such large volume that complete oxidation would not take place.

In filtering the lead peroxide it is necessary to add some paper pulp to the filter, otherwise some of the precipitate will run through. Should manganese be present, the lead will have to be determined by the sulphate method as the oxide of manganese would be precipitated with the lead peroxide and would not dissolve in the sulphuric acid added.

While we have not made many experiments, we feel safe in saying that the manganese could be separated directly from the copper sulphide filtrate, if most of the sulphuric acid is neutralized and the solution oxidized with ammonium persulphate.

In determining lead by the sulphate method or by the electrolytic method, a large amount of time is consumed in evaporating

[1] Andrews: This Journal, 17, 872.

to sulphuric fumes or in the long passage of the electric current, while by the titration method, if lead only is wanted, it may be determined without separating the tin, and the time required will be about thirty minutes.

If the copper is determined by the volumetric method, tin, lead, and copper results will be obtained in about one hour.

The following lead results were obtained on the same samples by the sulphate and volumetric methods.

Sample.	Sulphate method.	Volumetric method.
Bronze No. 4	2.60	2.61
" " 2	4.68	4.71
" H	5.05	4.97
" No. 1	5.39	5.33
" A	5.67	5.62
" B	7.47	7.51
" M	9.77	9.73
" S	13.72	13.62
" A.P	26.68	26.55
Babbit C	3.29	3.41
" D.S	65.85	65.93
" L	80.80	80.73
" D	89.63	89.50

We have lately had occasion to determine sulphur in bronzes and we have done this by dissolving about 10 grams of the sample in the double chloride of potassium and copper used in carbon determinations, filtering off the sulphide of copper and igniting to copper oxide. We then calculate the sulphur from the weight of oxide found; of course, in very accurate work the copper sulphide should be oxidized and the sulphur determined as barium sulphate.

Following are some analyses made by the methods outlined in this paper. All precipitates obtained were tested and in no case were impurities found.

	Babbit.	Babbit.	Bronze.	Bronze.	Bronze.	Bronze.
Tin	4.13	43.27	7.41	4.85	7.88	3.55
Lead	79.30	43.63	9.73	2.80	5.05	5.87
Copper	....	0.56	82.09	90.31	85.68	86.23
Antimony	16.30	12.60	....	....	....	....
Zinc	....	....	0.95	....	1.46	3.55
Manganese	....	....	....	1.80	....	....
Iron	....	....	....	0.21	....	0.40
Sulphur	....	....	....	....	....	0.30
	99.73	100.06	100.18	99.97	100.07	99.90

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SILVER AS A REDUCING AGENT.

By W. S. Hendrixson.

Received March 24, 1903.

As has been pointed out, silver, in a finely divided condition, is dissolved by ammonia in the presence of atmospheric oxygen, and it slowly reduces a neutral solution of potassium permanganate.[1]

It occurred to the writer that it might be of interest to study in a systematic and quantitative way the behavior of finely divided silver toward substances that readily give up oxygen, such as chromic, chloric, bromic, iodic and permanganic acids. Thus far the action of silver on chromic, chloric and iodic acids has been studied and the results and related problems are of sufficient interest to make the author desirous of studying the subject somewhat exhaustively. It is deemed best, in view of the absence of aid and the small amount of time at his disposal, to give some of the results in this preliminary statement and reserve the details for a future communication.

Three separate preparations of silver were made, two from the ordinary commercial nitrate, and one, which was used in most of the following experiments, from pure silver obtained by the method of Stas. In each case the silver was precipitated from an alkaline solution of silver oxide by formaline. It was washed and heated alternately with ammonia and dilute sulphuric acid, and washed until every trace of the acid was removed. The preparations were dried and heated at various temperatures, from 125°, in one case, to low red heat in another.

Action of Silver on Chromic Acid.—A solution of potassium bichromate was prepared by weighing the salt which had been obtained by crystallizing three times from water the chemically pure salt of commerce, and drying to constant weight. The salt was heated for two hours in a porcelain crucible in an air-bath at 120°, and then during two-hour periods at 150°, 170°, 200° and 300°. The crucible was then placed upon a triangle in a large porcelain crucible which served as an air-bath and which was heated with the full burner flame for two hours, when the salt showed incipient fusion. Its weight remained perfectly constant above 200°, and 17 grams lost only a few milligrams above 120°. From this salt

[1] M. Carey Lea: *Ztschr. anorg. Chem.*, **3**, 180.

and water obtained by fractionally distilling ordinary distilled water, a fifth-normal solution with respect to its oxidizing power was made, containing 9.8166 grams to 1 liter.

Weighed amounts of silver, about 1 gram in each case, were heated, sometimes in a covered beaker and sometimes in a flask with an air-cooling tube ground into its neck, with 25 cc. of the chromate solution and the same volume of normal sulphuric acid. Heated to gentle boiling, the time necessary for the complete reduction of the chromate varies much with the fineness of division of the silver. With silver used in the first two experiments the reduction was complete in fifteen minutes, while that used in 3, 4, and 5 required much longer. After the reduction was complete, the remaining silver was weighed in a Gooch crucible.

Following are the results of five experiments. The theoretical value is, of course, based upon the supposition that 1 molecule of chromate oxidizes 6 atoms of silver.

	Volume of bichromate. cc.	Silver dissolved.	Theory.
1	25.00	0.5413	0.5397
2	25.00	0.5428	.....
3	25.00	0.5380	.....
4	25.00	0.5366	. ...
5	25.00	0.5376	.....

Action of Silver on Iodic Acid.—In experiment 6 the iodic acid and silver were heated with normal sulphuric acid and in 7 the iodic acid was in water solution. After heating at the boiling-point for about two hours, replacing the water evaporated from time to time, the undissolved silver, silver iodate and iodide were weighed. So much of the mixture as possible, without getting asbestos from the Gooch crucible, was transferred to a porcelain crucible, weighed and heated to redness. Oxygen was evolved and was determined by loss. From the loss of oxygen in a portion of the mixture, the silver as iodate could be calculated, and from this, the silver in solution and the silver taken, the silver as iodide could also be calculated. In the following, column 1 shows the silver used, 2 the total loss of oxygen, 3 silver as iodate, 4 silver in solution, and 5 silver as iodide.

	1.	2.	3.	4.	5.
6	1.3700	0.1418	0.3188	0.0434	0.0727
7	1.0225	0.1508	0.3390	0.0008	0.0727

In experiment 6, the ratio of silver as iodide to the total silver oxidized is 1 : 5.98 and in 7 the ratio is 1 : 5.67.

Action of Silver on Chloric Acid.—In experiment 8, 7 cc. of Merck's chloric acid were diluted to 50 cc., and such a solution was about three-tenths normal. The acid contained only a trace of hydrochloric acid, too small an amount in the volume taken to influence the result. In experiment 9, normal sulphuric acid and pure potassium chlorate were used. After heating about two hours, the silver in solution and the residue of silver and silver chloride were determined.

	Silver taken.	Silver in solution.	Silver as chloride.
8	2.0295	0.8859	0.1775
9	1.9517	0.5514	0.1473

In experiment 8, the ratio of the silver as chloride to the total silver acted upon is 1 : 5.99 and in 9 the ratio is 1 : 4.74.

The experiments show that both chromic and iodic acids are capable alone of oxidizing large quantities of finely divided silver. Both acids seem to react quantitatively upon silver with the result that a molecule of the acid is completely reduced and 6 atoms of silver are oxidized, 1 of which forms a halide and 5 form silver chlorate or iodate as shown in the equation

$$6Ag + 6HClO_3 = AgCl + 5AgClO_3 + 3H_2O.$$

The action goes on in very dilute solutions. Calculations from the amounts of acids used and silver oxidized show that the strength of the iodic acid solution, when the experiment was stopped in experiment 7, could not have exceeded one-twentieth normal, and the strength of the chloric acid at the end of experiment 8 was about one-tenth normal. Bromic acid also readily dissolves silver but this reaction has not yet been quantitatively studied.

Action of Dilute Sulphuric Acid on Silver.—M. Carey Lea[1] has stated that even very dilute sulphuric acid dissolves, in small quantity, finely divided silver. I found this to be true in the case of every sample of silver prepared, and the amounts dissolved by the normal acid alone were determined. The weights of silver dissolved were in two samples about 0.4 milligram for each gram of silver taken, amounts so small that no corrections were made in experiments 1 to 8. A correction was, however, applied in experiment 9 in which the silver used was much more soluble.

[1] *Loc. cit.*

Since it was observed that continued heating did not seem to influence the amount of silver which the acid alone dissolved, a study was made of the reason for this solvent action. About a gram of silver on which the acid exerted a marked solvent action, was placed in a hard glass tube which was stoppered into a distilling flask so that the tip of the tube was in the bulb of the flask.

Through the tube and flask, which contained normal sulphuric acid and was placed horizontally, was passed pure hydrogen and the acid was boiled to expel any dissolved oxygen. The silver was heated in the current of hydrogen to reduce any oxide that it might contain. When cool it was allowed to fall into the boiling acid by tilting the flask and tube. By depressing the neck of the flask, small portions of the acid could be drawn off through the side tube from time to time and tested for silver. Though the evaporation was continued practically to dryness, no trace of silver was found in solution.

To determine whether the apparent solvent action might not be due to superficial oxidation of the silver, the above experiment was repeated, save that the silver was not heated. Again after long boiling no silver was found in solution. It then seemed of interest to determine at least approximately at what concentration boiling sulphuric acid begins to attack silver. The experiment was repeated save that the silver was not heated, and pure, dilute acid of the ordinary reagent strength was used. The acid was allowed to concentrate by evaporation and was, toward the end of the experiment, tested for silver at least every minute. Suddenly the character of the boiling changed and the silver rose to the surface and appeared spongy, owing to the formation of sulphur dioxide. The boiling was stopped and a test showed silver in solution. The acid was allowed to cool, a portion of it was weighed and titrated, and it showed a concentration of 74.03 per cent.

The above experiment seems to show definitely that dilute sulphuric acid alone is incapable of dissolving finely divided silver, and that the seeming solvent action is due to the oxygen of the air, oxygen dissolved in the acid, or to that derived from some external source.

In the near future an attempt will be made to ascertain whether, by excluding extraneous oxygen, the actual oxidizing power of a

bichromate solution may not be very accurately determined with silver.

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March 21, 1903.

REDUCIBILITY OF SOME METALLIC OXIDES BY HYDROGEN AND CARBON MONOXIDE.

BY IRVING W. FAY AND ALBERT F. SEEKER.

Received April 11, 1903.

IN passing hydrogen gas over silver oxide in a bulb tube to show the reduction of the oxide to metallic silver I frequently noticed slight explosions and a sudden change of oxide to metal at what seemed a low temperature for such an effect. In the literature, I found that silver oxide was reduced by hydrogen at 85°[1] and 100°.[1] Wishing to test the accuracy of these temperatures, the following investigation was begun with the impression that both temperatures were too high. Both hydrogen and carbon monoxide were used to reduce the silver oxide. Later, other oxides were submitted to the reducing action of these two gases.

The method used by Mueller[2] consisted in placing a glass tube containing the oxide in the sand of a sand-bath. A thermometer was thrust into the sand so that the bulb was close to the part of the tube containing the oxide. The tube was bent at a right angle, one end sealed, the open lower end dipping under water. The tube was filled with hydrogen and the temperature increased. Reduction of the oxide was shown by ascent of water in the open end or arm of the tube.

Wright[3] and Luff placed the metallic oxides for reduction in a test-tube arranged vertically in a paraffin bath, about 0.5 gram being taken for each observation. The mouth of the test-tube was closed by a cork with three perforations, one for the thermometer, the bulb of which reached to the bottom of the tube, one for the entrance tube for leading in the pure gas, and the third for an exit tube just passing through the cork and bent at a right angle and coupled by a rubber joint to a Will and Varrentrapp's ammonia

[1] Wöhler: *Ann. Chem.* (Liebig), **30**, 4.
[2] Müller: Pogg. *Ann.*, **136**, 51.
[3] *J. Chem. Soc.* (London), **33**, 1.

bulb apparatus filled with clear baryta water. In order to make sure that the entering gas was at the same temperature as the bath, the entrance tube was bent over, downwards and upwards, so as to form a U, reaching down to the bottom of the test-tube and lying close to the outer surface; the upper part of the tube was wrapped with lamp-wick to prevent aerial cooling. Loss of weight was used to determine actual reduction, and fifteen minutes was the time allowed for each test.

Experimental Part.

Reduction of Silver Oxide by Hydrogen.

The oxide was that sold as chemically pure. As a preliminary test, silver oxide was placed in a tube about 0.25 inch internal diameter, so bent that it was easily clamped in position with the bend 1 inch below the surface of oil in an oil-bath. A thermometer was hung in the oil with its bulb close to the bend of the glass tube where the silver oxide lay. Hydrogen gas from zinc and hydrochloric acid without drying was passed slowly over the oxide. At a temperature of 100°, the oxide was reduced in a few minutes to the familiar grayish white powder of metallic silver. An hour's heating at 80° did not seem to reduce any oxide, but examination under a microscope showed metallic silver in the dark powder. At 40° the microscope revealed particles of silver. The silver oxide had previously been examined under the microscope, and metallic silver proved absent. Below 40° no reduction was apparent, but, suspecting that longer exposure to hydrogen would show a reduction, a quantity of oxide was sealed in an atmosphere of hydrogen within a tube and laid aside in a drawer at ordinary laboratory temperature. At the end of a week, the black color of the oxide was completely changed to white metallic silver, and moisture could be seen upon the glass inside of the tube. A similar tube similarly charged was placed alongside a block of ice in a refrigerator. In a week, the powder had become blacker, and moisture was shown by the powder sticking to the tube, and metallic silver was seen under the microscope.

To insure the constant maintenance of 0° C. during the test, a wooden V-shaped trough was used, 1 foot in length and about the same in height. The tube containing the oxide lay along the

bottom of the trough, the end projecting through a round hole so bored as to allow of easy removal and insertion of the oxide tube. Crushed ice was kept in the trough, and woolen coverings were placed over it.

Pure dry hydrogen gas was used for the subsequent work. It was made from zinc and sulphuric acid, to which some copper sulphate solution had been added, and it was further purified by passing it in succession through two wash-bottles containing permanganate of potash solution, a U-tube containing pumice saturated with a solution of mercuric chloride, a U-tube filled with pumice wet with a solution of potassium hydroxide, a piece of iron pipe, containing copper tacks and copper gauze, heated to redness (the wrapped ends kept cool by water dripping from capillary tubes), a U-tube containing anhydrous copper sulphate, a tower of calcium chloride, and a wash-bottle half-filled with phosphorus pentoxide. The rubber joints were covered with shellac varnish.

A glass tube 0.5 inch internal diameter was charged with silver oxide, and capillary tubes were drawn out at each end. The tube was placed in the ice trough and, when some time had elapsed to allow it to attain 0° C., a stream of hydrogen was passed for one hour, and then a manometer tube consisting of a capillary tube of U-shape half-filled with mercury and so bent that the parallel arms were but an inch apart, the height of the manometer being 12 inches, was joined to the oxide tube by a short, tightly-fitting black rubber tubing, afterward covered with shellac varnish.

The capillary where the hydrogen had entered was sealed, and except for additions of ice from time to time, the apparatus was left to itself for five days. The progress of the reduction is shown in the following table of corrected readings.

Rise of mercury in the arm toward the oxide tube:

	mm.
End of 6 hours	7.6
" " 1 day	24.0
" " 2 days	35.8
" " 3 "	47.8
" " 4 "	56.4
" " 5 "	70.4

On removing the tube from the melting ice, moisture was plainly visible condensed on the upper side.

The amount of reduction was so much more than was expected

that it was feared hydrogen had diffused outward through the rubber joint, and thereby increased the apparent reduction. Another tube was prepared to test this by having the oxide tube and the capillary manometer entirely of one piece of glass. A long capillary tube was drawn out from the end of an 8-inch glass tube; it was then bent at a right angle and turned in U-shape, the parallel arms close together; another very short capillary was drawn out close to where the manometer capillary joined the main tube; this short second capillary on the same end as the manometer allowed a continuous stream of hydrogen to pass without disturbance of the mercury in the manometer. This tube was charged along the bottom with silver oxide, the open end drawn out to a capillary and then placed in the ice trough to acquire 0°.

A stream of pure dry hydrogen was passed for one hour, and several times the tube was rocked in such a manner as to bring the mercury close up to the short capillary, through which hydrogen was passing. This accomplished the expulsion of all air in the branch of the manometer tube next the oxide. The capillaries at both ends were sealed and the tube maintained at 0° for twelve days by an abundance of ice and careful covering.

The amount of reduction day by day was as follows:

	mm. corrected.	
End of 6 hours	5.6	
" " 1 day	14.9	
" " 2 days	18.3	
" " 3 "	36.1	During the sixth day the apparatus was placed out of doors, when the temperature was 20° below freezing.
" " 4 "	39.0	
" " 5 "	51.1	
" " 7 "	67.9	
" " 8 "	68.5	
" " 9 "	78.9	
" " 10 "	88.8	
" " 11 "	94.5	
" " 12 "	107.2	

Auric oxide, subjected to exactly similar treatment with hydrogen gas at 0°, showed a more rapid reduction than silver oxide, as the following table will show.

	mm.
End of 6 hours	67.8
" " 1 day	73.9
" " 2 days	66.4
" " 3 "	73.5
" " 4 "	80.0

In all of these tests the surface-tension of the mercury in the capillary manometer was such that movement was sluggish, and the tube needed frequent tapping to cause a readjustment of the mercury column.

REDUCTION OF THE OXIDES OF MERCURY BY HYDROGEN.

The oxide was placed in a glass tube 0.25 inch inside diameter, bent at such an angle that the bend itself was 1.5 inches below the surface of oil in an oil-bath, in which it was heated. At first, on passing the hydrogen, the temperature was rapidly increased until the oxide could clearly be seen to exhibit reduction. A thermometer was hung in the bath with its bulb close to the bend of the tube where the oxide lay. To determine the lowest temperature at which six hours' contact with hydrogen would show reduction, tests were made with fresh portions of oxide at each interval of 5° below the temperature discovered in the above process, and reduction proved by the vacuum formed within the tube. Each test was as follows: The ends of a glass tube 0.5 inch in diameter and 6 inches long were drawn out to capillary tubes 3 inches long. The oxide was introduced and spread along the bottom of the tube and a large excess of pure hydrogen passed through. Both capillaries were sealed and bent upward to allow of immersion in an oil-bath of moderate size. A constant temperature was maintained by a thermostat, and careful protection of the flame and bath from drafts. Any reduction at the end of the six hours' heating revealed itself by a partial vacuum formed within the tube when cooled to its original temperature.

To ascertain the presence of a slight vacuum and therefore of the slightest reduction of the oxide, a manometer was used, consisting of two capillary glass tubes fastened side by side to a millimeter scale, their lower ends joined by rubber tubing. The oxide-tube to be examined was connected by a small rubber tube to one arm of the manometer, *i. e.*, the capillary tube, scratched with a file near the tip, was thrust into the rubber tube, the other end of which was joined to one arm of the manometer. The mercury in both arms was brought to a level, the tip of the oxide tube broken off within the rubber tube, and any partial vacuum was at once revealed by a rise of the mercury in the arm of the manometer next to the oxide-tube. Blank tests made at different times showed

the largest error due to manipulation to be 5 mm. No metallic oxide was regarded as showing reduction unless the corrected vacuum attained exceeded 5 mm. The lowest temperatures for the reduction of the oxides of mercury are as follows:

Mercurous oxide	80° C.
Yellow mercuric oxide	150° C., at 130° C.[1]
Red mercuric oxide	115° C., at 230° [1]

REDUCTION OF SOME METALLIC OXIDES BY CARBON MONOXIDE.

The method consisted in passing pure dry carbon monoxide over the metallic oxide charged in a bent glass with the bend immersed 1.5 inches below the surface of the oil in an oil-bath. The thermometer bulb was fixed close against the bend of the immersed tube where the oxide lay. A constant temperature at any degree was secured by a thermostat, and protection of the flame and oil-bath from drafts. Any carbon dioxide formed by reduction of the metallic oxide was detected by passing the gas through a Marchand tube, containing a solution of barium hydroxide.

The carbon monoxide was made from coarsely crushed potassium ferrocyanide and concentrated sulphuric acid. Raising the temperature rapidly until evolution of the gas began and then lowering the flame, gave perfect control of the gas, which otherwise may be given off tumultuously. The gas was purified and dried by passing it through a train consisting of two wash-bottles of solutions of sodium hydroxide and one of lime-water, a tower of calcium chloride, and a wash-bottle half-filled with phosphorus pentoxide. The barium hydroxide solution, one-third the strength of saturation, was shaken with barium carbonate to increase its sensitiveness to carbon dioxide. This solution was found sensitive to the carbon dioxide in 0.25 liter of atmospheric air, which is 0.075 cc. Lime-water was much less sensitive, requiring 0.75 liter of atmospheric air to give an equal amount of turbidity in the same volume of liquid. Efficiency of the purifying train was proved by making blank tests from time to time. The Marchand tube containing the solution of barium hydroxide was protected from backward diffusion of carbon dioxide from the air by a second Marchand tube, charged like the first. Each test was continued for six hours, the gas passing at the rate of one to two

[1] Müller: Pogg. *Ann.*, **136**, 62.

bubbles per second, the temperature kept constant during the time. A first test was made sufficiently high to find where reduction actually took place with rapidity, then successive tests at intervals of 5°, until no turbidity was shown by the barium hydroxide solution. In reductions by carbon monoxide, a tendency clearly exists for the carbon dioxide formed to unite with unchanged oxide to form carbonate to some extent, but, with an excess of carbon monoxide passing, this, it is believed, could have but little effect upon the result.

The following shows reduction temperatures for carbon monoxide. (Time of test, six hours.) Silver oxide, 0°C.; auric oxide, 0°; mercurous oxide, 0°; yellow mercuric oxide, 0°; red mercuric oxide, 95°.

CONCLUSIONS.

(1) The minimum temperature of reduction of both silver and gold oxide by hydrogen is much below zero, and that for carbon monoxide lower than that for hydrogen.

(2) Carbon monoxide is a more rapid and efficient reducing agent than hydrogen.

(3) The differences in the temperatures of reduction of the yellow and red oxides of mercury make them exhibit properties of two different substances, and confirm the differences previously found in their behavior to chlorine,[1] oxalic acid,[2] iodic acid,[3] and ammonia.[4] Further work is being done with the oxides of lead and copper.

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NOTES.

Analysis of Water from Hinton, West Virginia.—This water is characterized by a large content of manganese, nickel and cobalt salts. In many mineral waters, manganese salts are reported as present in traces or in comparatively small quantities, but in this water the amount of manganese salts is so large that during evaporation a very marked brown precipitate of a

[1] Pelouze: *Compt. rend.*, **16**, 50.
[2] Millon: *Ann. Chem.* (Liebig), **18**, 349.
[3] Rammelsberg: Pogg. *Ann.*, **44**, 570.
[4] Hirzel: *Ann. Chem.* (Liebig), **84**, 258; Weil: Pogg. *Ann.*, **123**, 358.

manganese compound is formed, part of which floats on the surface of the evaporating water. This precipitate dissolves on the addition of hydrochloric acid with the evolution of chlorine in such quantity that the evaporation of the acidified water to dryness cannot be made in a platinum dish.

The relative quantity of manganese salts in this water is greater than that in any of those given in Peale's[1] Mineral Springs of the United States, while the quantity of the nickel and cobalt salts is only exceeded by the amounts in the waters of the Jordan[2] Alum and Rockbridge Alum Springs, Virginia.

Still larger contents of manganese, nickel and cobalt salts are found in the water of Roncegno,[3] South Tyrol.

The specific gravity of the Hinton water at 15°-16° was 1.007.

The weight of solids dried at 180° was 1.2836 grams per liter, or 74.9750 grains per U. S. gallon.

The results of the analysis were:

	Parts to 1,000,000.
Potassium (K)	4.6
Sodium (Na)	306.7
Calcium (Ca)	89.6
Magnesium (Mg)	42.4
Aluminum (Al)	1.3
Iron (Fe)	10.5
Manganese (Mn)	40.7
Nickel and cobalt (Ni, Co)	3.6
Silicate ion (SiO_3)	16.0
Carbonate ion (calculated) (CO_3)	109.1
Chlorine (Cl)	627.2
	1251.7

This corresponds to:

	Grams per liter.	Grains per U. S. gallon.
Potassium chloride	0.0087	0.5082
Sodium chloride	0.7785	45.4722
Calcium chloride	0.1776	10.3736
Magnesium chloride	0.0847	4.9473
Magnesium carbonate	0.0710	4.1471
Alumina	0.0024	0.1402
Silica	0.0128	0.7476
Ferrous carbonate	0.0215	1.2558
Manganese carbonate	0.0848	4.9532
Cobalt and nickel carbonates	0.0073	0.4264
	1.2493	72.9716

W. G. BROWN.

[1] Bulletin of the United States Geological Survey, No. 32.

[2] *Loc. cit.*, pp. 62 and 65.

[3] Gläser und Kalmann: *Ber. d. chem. Ges.*, **21**, 1637 and 2879; abstract in *J. Chem. Soc.* (London), **54**, 796 and **56**, 28.

NEW BOOKS.

ON THE "BECKMANN REARRANGEMENT." BY JULIUS STIEGLITZ, Professor of Chemistry in the University of Chicago. Chicago: University of Chicago Press. Price, 25 cents.

This is a carefully prepared monograph on the probable cause and mechanism of the "Beckmann Rearrangement," which is so defined as to include a variety of reactions in which an alkyl or alphyl group leaves a carbon atom to attach itself to a neighboring atom of nitrogen, as well as the corresponding rearrangement in the case of oximes. The author, after arriving at the conclusion that "The interpretations of the rearrangement given by Hoogewerff and van Dorp, Hantsch, Beckmann, Hesse, Freundler, and Nef do not agree with all the established facts," advances evidence in support of the view, that "All the most important results of the investigations of the reaction from the point of view of the constitution of the substances involved, agree best with an interpretation which postulates the intermediate formation of a univalent nitrogen derivative as the essential cause of the rearrangement".

S. P. MULLIKEN.

THE ANALYSIS OF OILS AND ALLIED SUBSTANCES. BY A. C. WRIGHT, M.A., B.Sc. New York: D. Van Nostrand Co.; London: Crosby, Lockwood and Son. 8vo. Cloth, 241 pp. Price, $3.50 net.

This book describes very fully the various constituents of oils, waxes and resins and also the methods of the determination of the physical and chemical properties of these bodies. It discusses further the treatment of the non-fatty matters contained in oils and gives the means of their identification and estimation. This is followed by the description, properties and methods of investigation of the important oils, fats and waxes, some fifty in number. The work concludes with the examination of some commercial products, as turkey-red oils, lubricating oils and greases, and paint oils.

The treatise, which may be tersely described as an abridged Lewkowitsch, is most admirable, and will doubtless replace it in many cases. There are, however, some statements which are not in accord with the usual experience, particularly that the open flash test of oils is better than the closed. In some instances the

methods are not explained with sufficient clearness; one is in doubt, for example, as to the procedure to be followed in the estimation of free acid.

In view of the fact that all references are so far as "possible to the *Journal of the Society of Chemical Industry*, to which practically all chemists and students have access," it would seem to be of doubtful expediency to introduce into this book processes there given, the results of which are open to question, such as Farnsteiner's method for the separation of oleic acid. While the writer cordially concurs in the exclusion of some tests—particularly color tests—yet he feels that it was a mistake not to have included McIlhiney's bromine test, one of the most valuable in the examination of these compounds. The omission of the satisfactory David's test for rape seed oil is also to be noted. No mention is made of corn or peanut oils, although maize and earthnut oils are carefully described; the treatment of linseed oil is particularly satisfactory.

Mineral oils, except as adulterants, are not discussed, although a description of the flash and viscosity tests is given. The usefulness of the work would be increased were the index more complete. It is a valuable book and may be warmly recommended to those interested in the subject. A. H. GILL.

A HISTORY OF HINDU CHEMISTRY FROM THE EARLIEST TIMES TO THE MIDDLE OF THE SIXTEENTH CENTURY A. D. With Sanskrit Texts, variants, translation and illustrations. BY PRAPHULLA CHANDRA RAY. Vol. I. London and Oxford: Williams and Norgate. 1902. pp. i-iii, a-d, i-lxxix, 1-176, 1-41. 7 plates. 8vo. Price, 12s, 6d.

The author, who occupies the chair of chemistry in Presidency College, Calcutta, has done for Hindu chemistry what Berthelot did a few years ago for Greek, Arabic and Syriac documents of the Middle Ages. His historical studies begin with the sacred books of very early, uncertain dates, and extend to about the year 1550 A. D.; the second volume will probably bring the subject down to the present time. In the Atharva-veda, the Charaka and the Susruta, occur the earliest references to therapeutical and chemical knowledge, as well as to pharmaceutical preparations; they date probably prior to the fifth century. In these and succeeding writings, alchemical ideas abound, mixed up with magic, sorcery, and religious rites of a debasing character. The chief of these were

known to the Arabians at an early date and furnished them with a large part of the chemical skill with which they are usually credited.

Hindu ideas concerning the constituion and properties of matter resemble in many points the philosophy of the early Greeks, and it has been suggested that the latter were influenced by Indian thought through Persia. Almost all the doctrines ascribed to Pythagoras, mathematical, religious and philosophical, were known in India in the sixth century B. C.

The invention of the processes of calcination and distillation is ascribed to the renowned and venerable Nagarjuna, one of the twenty-seven alchemists named in the Rasaratnasamuchchaya, a famous work of the Iatro-chemical period. Another philosopher in physical science was Kanāda who propounded a doctrine similar, in many points, to the atomic theory of Democritus; his anticipations as respects the propagation of sound and the identity of light and heat excite wonder and admiration.

The volume contains summaries of the knowledge of the ancient Hindus concerning metals, salts, alkalies (the "good" and the "bad"), and of technical arts having a chemical basis, such as the manufacture of calomel, of saltpetre, as well as of metallurgical operations.

Zinc was recognized as a metal as early as 1374 A. D., long before pseudo-Basil Valentine, and Paracelsus.

The method of treating the refuse and wastage of goldsmith's workshops is described and explained in modern chemical language.

The claim is made that the Hindus knew how to prepare mineral acids earlier than Europeans.

To analyze the work more fully in the space that can be given is impossible; the whole book shows the erudition and careful study of an accomplished scholar, not only in chemistry but in Sanskrit as well, citations being given in this language.

An appendix contains several full page plates of furnaces, copper smelting, alum manufacture, etc.; also 41 pages of Sanskrit texts and two indexes, one to proper names and one to subjects [but why separated?].

The book bears internal evidence of having been printed in Calcutta, with clear type and on good paper. The second volume will be awaited with interest, and the two will form the standard

monograph on Hindu chemistry that will be indispensable in every library. HENRY CARRINGTON BOLTON.

THE TESTING OF CHEMICAL REAGENTS FOR PURITY. By DR. C. KRAUCH, chemist to the firm of E. Merck, Darmstadt. Authorized translation of the Third Edition by J. A. WILLIAMSON and L. W. DUPRÉ. With additions and emendations by the author. London: Maclaren & Sons; New York: D. Van Nostrand Co. 350 pp. 1903. Price, $4.50 net.

To prescribe a series of tests of chemical reagents which should be sufficiently detailed to cover their use in all sorts of highly specialized cases would be well-nigh impossible. The general and many of the special applications of the inorganic reagents and of such organic substances as are employed as solvents, indicators, or for special tests are, however, well provided for in the material which Dr. Krauch has compiled from various sources, and to which he has added the results of his own experience. For each substance the Latin name, symbol, molecular weight, and a brief description are given, and these are followed by discussions of the tests for impurities, the methods of quantitative estimation, the uses of the reagent, precautions to be observed in connection with its storage, and a description of its commercial varieties. An appendix includes the preparation of ordinary reagents and of normal solutions, a discussion of reagents and reactions in general, and a table of atomic weights [which, however, bears the date, 1890].

The translation seems to have been faithfully carried out. It may be questioned whether it would not have been preferable to add the references to English works and journals to those in other languages, rather than to substitute them, since the reader may often prefer to consult the original papers. The Lunge and Isler table for the strength of sulphuric acid at various densities is stated on page 309 to be more reliable than that of Kolb and it would seem that it should replace the latter table in this work.

To many who have found the German edition of Dr. Krauch's book a valuable assistance, this translation will need no endorsement; to others it can be recommended as a guide in determining the extent to which freedom from impurities in reagents may reasonably be expected, and in the selection of methods of testing.

H. P. T.

LEAD AND ITS COMPOUNDS. By THOMAS LAMBERT. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1902. 228 pp. Price, $3.50.

Some seventy pages of this book are taken up with a description of the dressing of lead ores and the metallurgy of lead.

A chapter on lead oxides and their manufacture follows, and fifteen pages are devoted to substitutes for white lead. A brief account of the metallurgy of zinc follows, including a description of compounds used as pigments, and of pumice stone, china clay, etc.

Drying oils, siccatives and turpentine are briefly discussed. A classification of mineral pigments and a chapter on the analysis of raw and finished products close the book. The tables at the end are of little moment.

Inasmuch as this book contains nothing which is not more fully and authoritatively treated in other easily accessible works, it can be of little use to the American chemist or metallurgist, but is evidently designed to contain general information of interest to those engaged in the manufacture of paint from lead and zinc compounds. WM. HOSKINS.

TESTS AND REAGENTS, CHEMICAL AND MICROSCOPICAL, KNOWN BY THEIR AUTHORS' NAMES, together with an Index of Subjects. By ALFRED I. COHN, PH.G. New York: John Wiley & Sons. 1903. 8vo. Cloth. 353 pp. Price, $3.00.

The object of this book, as stated by its author, is "To supply the busy chemist, microscopist, and pharmacist with data which are frequently desired, but which are often not at hand or are inaccessible." The tests and reagents are arranged alphabetically under the names of their originators. Their number is estimated to be not far from 2,500. The descriptions are necessarily all very compact, but the work of condensation has been well done—a fact which in a measure compensates for the usual omission of bibliographical references.

The following selected topics will serve to illustrate the nature of the matter abstracted: Hager, "Test for Dextrine in Acacia"; Halphen, "Cottonseed Oil"; Hammersten, "Indican in Urine"; Haug, "Decalcification Solution"; Hefelmann-Mann, "Fluorine in Beer"; Hayem, "Solution for Fixing Blood Corpuscles."

The book is especially complete in its list of tests and reagents

employed in pharmaceutical and medico-chemical practice, but contains much to make it a useful addition to the library of any analyst. Its value is greatly enhanced by the addition of the alphabetical subject index. S. P. MULLIKEN.

VORLESUNGEN ÜBER THEORETISCHE UND PHYSIKALISCHE CHEMIE. VON J. H. VAN'T HOFF. Zweites Heft. Die Chemische Statik. Zweite Auflage. Braunschweig: Friedr. Vieweg und Sohn. Ladenpreis, geheftet, Mk. 4.

The second edition of the second part of this set of lectures differs very slightly from the first edition, the differences being mainly in choice of illustrative examples cited in the text, for which recognition of more recent work calls, and in the increased number of references. The chapter on solid solutions is the most conspicuous in both respects. A few typographical slips occur in the second edition which do not appear in the first, and curiously enough the second edition omits the references to Brunis' work (pages 68 and 70) mentioned in the text, though the reference is given in the first edition. The leading of the tables in the second edition seems to be an improvement, and the press work as a whole is quite satisfactory. The few changes made in this new edition of a well-known work do not justify any extended or detailed notice, but the opportunity can not be passed of insisting upon the great value of this work to the general chemist.

Considering chemical statics under the three general headings, Molecular Weights, Molecular Structure, and Molecular Grouping, the author has discussed the modern theory of solutions, gaseous, liquid and solid, stereochemistry, and physical crystallography, subjects usually treated as widely variant in character, and with but incidental points of contact, but which are here brought into a comprehensive whole. There are probably few indeed who will not find their menta! horizon considerably widened by the careful reading of this volume, and with its two companion ones on "Chemical Dynamics" and "The Relations between Properties and Composition" it should well repay an occasional re-reading. FRANK K. CAMERON.

ELEMENTS OF PHYSICS. BY ERNEST J. ANDREWS and H. N. HOWLAND. With Manual of Experiments. New York: The Macmillan Company. 1903. Price, $1.10 net.

The general plan of this new addition to the large number of

elementary texts on physics is "to eliminate a few subjects which have no practical bearing, and the relations of which to the fundamentals cannot weli be made apparent; to present difficult subjects fully and in simple terms; and to connect each subject, directly or indirectly, with every other by fundamental principles or their corollaries."

This plan has been carefully and conscientiously followed and the resulting book is on the whole to be recommended. The weakest part is the "Manual of Experiments," but as most schools use a separate manual, this cannot be accounted a serious defect.

C. E. LINEBARGER.

A TEXT-BOOK OF ORGANIC CHEMISTRY. By DR. A. F. HOLLEMAN. Translated from the Second Dutch Edition by A. JAMIESON WALKER, PH.D., assisted by OWEN E. MOTT, PH.D., and with the coöperation of the author. New York: John Wiley & Sons. 1903. 72 figures. Cloth. 8vo. xvii + 555 pp. Price, $2.50.

The purpose of the author is to bring out distinctly the underlying principles upon which the division of the subject is based, the experimental proof for the constitutional formulas assigned, the bearing of physico-chemical theories upon the problems of organic chemistry, and the like, rather than to describe a large number of compounds or record a confusing mass of isolated facts; in a word, to provide a text-book which should give a clear presentation of the theoretical aspects of organic chemistry, rather than a condensed "Beilstein." The author's purpose has been carried out with very satisfactory results in the present work, an excellent text-book, widely and favorably known, this new edition being as nearly up-to-date as can reasonably be expected of any text-book. A second German edition has already appeared of the work, and an Italian translation is in preparation; English-speaking students will therefore be grateful to Messrs. Walker and Owen for this translation of the latest Dutch edition. The publishers' work is well done, the book being gotten up in very attractive form, clearly printed on good paper.

MARSTON T. BOGERT.

SIDEROLOGY: THE CONSTITUTION OF IRON ALLOYS AND SLAGS. By HANNS FREIHERR VON JUPTNER. Translated from the German by CHARLES SALTER. London: Scott Greenwood & Co.; New York: D. Van Nostrand Co. 1902. viii + 344 pp. Price, $5.00.

The original edition of this book has been reviewed in this

Journal (**23**, 117); in the present review we shall speak only of the translation. The translator has proved the exception to all rules, and has omitted a preface of his own. Perhaps under the circumstances it would be well to be charitable, and forgive some of the faults of the book, inasmuch as we are not informed of the conditions under which it has been produced. It is impossible, however, not to mention some of them.

The translation is similar to the original in all respects, with the single exception of the valuable bibliography which appeared at the end of the original. This has unfortunately been omitted in the translation. In the second volume the author included much valuable material on the application of the phase rule to the equilibrium phenomena of iron and carbon, which had been published by Roozeboom, Le Chatelier, and others after the first volume had appeared. As this will, ultimately, be included as part of the first volume by Jüptner, it seems a great pity that the translator did not see fit to incorporate it in its proper place.

On reading carefully through the book one is confronted by many inaccuracies, either original or copied from the German edition, which seems to indicate that the translator has not brought that love of duty, and knowledge of his subject to his aid which would provide a translation worthy of the original. It would be idle to mention all of the mistakes noticed, but some of the most striking will be referred to.

In regard to proper names, we find on page 10, *Gouthrie,* which should read Guthrie, copied from the original; on page 86, Sorby reads Storby; and E. D. Campbell appears in several places bearing the initials E. W. The terms inter-crystalline and inter-granular which originated with Stead in England, reappear in English as *intra*-crystalline and *intra*-granular; crystallites become crystalliths. In the text the spelling pearlite is used, while the German *perlite* is used to designate the micrographs of this constituent.

The translation of some of the German words is particularly unhappy. Speaking of boring steel under water to collect the gases, anbohren is translated *broached;* uebergiesst as *suffuses;* zerhacktes as *hacked-about;* Glimmer ähnlich Blättchen as scales *analogous* to mica; gedacht, as *imagined;* Bestandtheile, as *compound.* Many other such mistakes are noticed.

It is to be regretted that so many evidences of carelessness are noticeable, but even with these the book is sure to be welcomed by those who are unable to read the original, and who are interested in the scientific treatment of the constitution of iron and its alloys. The book comes from the press in very attractive form, but the reviewer can see no reason why the reader should be forced to accept with it thirty-five pages of advertising matter. HENRY FAY.

PHYSICO-CHEMICAL TABLES FOR THE USE OF ANALYSTS, PHYSICISTS, CHEMICAL MANUFACTURERS AND SCIENTIFIC CHEMISTS. BY JOHN CASTELL-EVANS, F.I.C., F.C.S., Superintendent of the Chemical Laboratories and Lecturer on Inorganic Chemistry and Metallurgy, at the Finsbury Technical College. Volume I, Chemical Engineering and Physical Chemistry. London: Charles Griffin and Co., Lim.; Philadelphia: J. B. Lippincott Co. 1902. xxxii + 548 pp. Price, $8.00.

This volume contains not only what its title in the narrower sense denotes—the physical constants of chemical substances, but also the values of various mathematical functions and of the relations of units in different systems, data pertaining to materials used in construction, and tables of many original calculations made by the author with the purpose of facilitating reductions and corrections and avoiding interpolations or calculations from empirical formulas. Most of the important quantities are expressed both in English and in metric units. The principal physico-chemical constants included in this volume are specific volumes and gravities and heat-expansions; specific heat-capacities and heats of fusion, vaporization, and solution; compressibilities; vapor-pressures; boiling-points, and melting-points.

The two most striking defects of the book revealed by a cursory examination are the absence of references to the original literature and the utter disregard of the significance of figures; thus in the mathematical tables many functions are given with three to seven more digits than the corresponding argument, and in the physical tables compressibility-coefficients are given with three or four figures when the unit is the atmosphere, with seven when the unit is the kilo per square millimeter or the ton per square inch, and specific heat-capacities and vapor-pressures are given with six figures, though the results of different investigators vary greatly in the fourth figure, etc.

In spite of these defects the book contains an enormous mass of data

within a small compass and in a form ready for practical use, and it may therefore prove of considerable value to industrial chemists and to chemical engineers. Scientific workers, however, will undoubtedly still prefer to utilize the original values of physico-chemical constants so well reproduced in Landolt and Börnstein's Tabellen, and to obtain mathematical functions from some work, like Holman's excellent Computation Rules and Logarithms, devoted especially to them.

A. A. NOYES.

ANNUAIRE POUR L'AN 1903, PUBLIE PAR LE BUREAU DES LONGITUDES. Paris: Gauthier-Villars. 24mo. 666 + 96 pp. Price, 1 fr. 50.

One-half this annual is occupied by astronomical data, one-quarter by diverse information of the nature of a newspaper almanac, and the last quarter by miscellaneous physical and chemical tables. The latter are either so incomplete or so antiquated in their data as to be in most cases no better than none at all. Even in a table of gaseous densities contributed by Berthelot, are to be found such serious mistakes as mercury and cadmium vapors being given the formulae Hg_2 and Cd_2. Cheap book—unreliable information, at least as far as the physical and chemical tables are concerned.

J. W. RICHARDS.

A CATALOGUE OF THE LIBRARY OF THE CHEMICAL SOCIETY [OF LONDON]. Arranged according to authors with a subject-index. London: 1903. 12mo. 324 pp.

This excellently printed volume shows on every page due care in its preparation, will admirably serve the purpose for which it has been compiled, and will prove useful to all interested in the bibliography and history of chemistry. Those handling it should bear in mind that it is a catalogue of the books in a given place and not a bibliography, and the absence of a book of intrinsic merit must not be criticized. To condemn a catalogue for its omissions is hardly just, when all the compiler can do is to include the books on the shelves of the library even though he may feel the need of certain volumes more keenly than the members of the Society themselves do.

The compiler of this volume, Mr. Robert Steele, deserves the thanks of all chemists and librarians.

HENRY CARRINGTON BOLTON.